Identification and Control of Metal Pollutant Spikes in Municipal Solid Waste Incinerators

A Thesis

Submitted by

David J L Poole (MChem)

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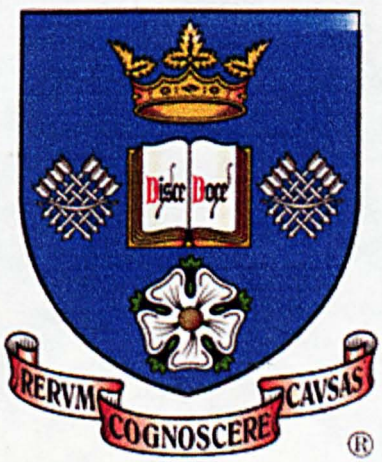

Department of Chemical and Process Engineering
The University of Sheffield

CONTAINS PULLOUTS

Summary

The emission of metals during municipal solid waste incineration has become a question of considerable public and scientific concern in the light of evidence of their extreme toxicity. Sophisticated and expensive gas cleaning systems are required to meet the increasingly stringent EC atmospheric emission limits. While the technology for the clean-up of particulate matter and acid gases in flue gas is comparatively straightforward, the emissions of micro-pollutants such as heavy metals and dioxins remain a concern. Previous research on metal emissions has concentrated on overall mass balances, working either with laboratory or plant based measurements, or with computational models (frequently with little correlation between the techniques), leading to incomplete information on the system concerned. The waste incineration process is highly inhomogeneous, due to the changing nature of the waste feed, but the effects of changing waste feed and combustion conditions on the concentration and distribution of metals in incinerator residues has not been investigated fully until now.

Therefore the main objective of this PhD research project was to develop a comprehensive understanding of metal behaviour during municipal solid waste incineration, including an assessment of the importance and effect of temporal variation in waste composition and incineration conditions, through a co-ordinated programme of experimental measurements and mathematical modelling.

A new on-line continuous monitoring technique was developed in order to obtain temporally resolved data on metal concentrations in incinerator flue gases. This system was used to obtain unique data on the distribution of nineteen different metals in a UK municipal solid waste incinerator. It was found that not only was metal distribution highly dependent on the volatility of the metal concerned, but also that temporal fluctuations could be extremely significant. These were caused by changing waste feed and changing incinerator conditions.

In parallel with the experimental programme, state-of-the-art thermodynamic modelling techniques were used to predict the distribution of metallic pollutants during waste incineration, for a range of waste compositions and combustion conditions. The thermodynamic equilibrium around various heterogeneous items in municipal waste was studied in order to a) assess the importance of non-uniformity in the waste stream, and b) investigate whether this could lead to the observed periodic changes in metal concentrations. These calculations, in conjunction with the experimental data obtained, have helped to show how unusual partitioning behaviour can be the result of local or transient behaviour on the burning bed, as well as changing bulk incinerator combustion conditions or bulk waste feed properties.

These two approaches to the problem of understanding metal behaviour during municipal solid waste incineration have complemented each other extremely well. The presence of spikes in metal emissions has clearly been demonstrated, and probable causes have been identified. Heterogeneous items containing high proportions of volatile metal are the most likely source of the large spikes observed for some heavy metals, whilst other changes are linked to more general incinerator conditions. These results indicate that more careful sorting of municipal waste prior to incineration could significantly reduce the toxic metal spikes in the flue gas, and therefore the overall environmental impact of incineration, although the atmospheric emissions are already near-zero and are therefore of minimal impact.

Dedication

"Moses saw that though the bush was on fire it did not burn up. So Moses thought, "I will go over and see this strange sight—why the bush does not burn up."

(Exodus 3: 2-3, The Bible)

Dedicated to all those who marvel at the world in which we find ourselves, and who through their investigation, come to realise that it is far too amazing and complex to have occurred by chance, and far too special to allow to go to waste. In their searching, may they find both the satisfaction of finding answers to their questions and solutions to their problems, and the peace which comes only from an encounter with the Creator of it all.

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AAS	Atomic Absorbtion Spectrometry
APC	Air Pollution Control
CCD	Charge Coupled Device
CEM	Continuous Emissions Monitoring
CEML	Continuous Emissions Monitoring Laboratory
COPD	Chronic Obstructive Pulmonary Disease
CPS	Counts Per Second
DEFRA	Department for the Environment, Food, and Rural Affairs (UK)
DL	Detection Limit. Also referred to as LOD (limit of detection)
EA	Environment Agency (UK)
EPA	Environmental Protection Agency (US regulatory body)
ESP	Electro-Static Precipitator
EU	European Union
GDE	General Dynamic Equation
GF	Graphite Furnace
ICP	Inductively Coupled Plasma
ID	Induced Draft
IPC	Integrated Pollution Control
Isokinetic	To remove a sub-sample from a fluid flow, at the same velocity as the bulk velocity of flow, thus obtaining a representative sample of gas and particulates
LIBS	Laser Induced Breakdown Spectroscopy
LOD	Limit of Detection (also referred to as DL – detection limit)
LOGS	Laser Opto-Galvanic Spectroscopy
MS	Mass Spectrometry
MSW	Municipal Solid Waste
NFFO	Non Fossil Fuel Obligation
OES	Optical Emission Spectrometry
PAHs	Polyaromatic Hydrocarbons
PCBs	PolyChlorinated Biphenyls
PCDDs	Polychlorinated dibenzo-p-dioxins
PCDFs	Polychlorinated dibenzofurans
PICs	Products of incomplete combustion
PMT	Photo-multiplier Tube
PPM	Parts Per Million
PVC	Poly Vinyl Chloride (a common plastic containing chlorine)
RSD	Relative Standard Deviation
SD	Standard Deviation
TLV	Threshold Limit Value (Standard for Toxin Maximum Exposure)
USN	Ultra-Sonic Nebuliser
XRF	X-Ray Fluorescence

Chapter One:

Introduction

1.1 Background

1.1.1 Municipal Solid Waste Incineration

Around 250 million tonnes of controlled (Household, Commercial and Industrial) waste are produced in the UK every year (Williams, 1998), and the difficult question of how best to deal with this unwanted material is one which must be addressed. Historically, the main disposal route for waste has been landfill, but it has been recognised that this disposal route is not sustainable, due to the lack of availability of space, not to mention scarcity of new resources. Difficult, subjective and possibly publicly unpopular decisions must be made, in order to reduce waste production, and optimise its disposal.

The current fundamental strategy adopted throughout the EU to handle this issue is the **hierarchy of waste management**. This strategy seeks to deal with waste in the best manner, with the order of preference being **reduction**, **re-use**, **recovery** or **disposal** (Williams, 1998): The best way to deal with waste is to minimise its production, through improved, higher efficiency industrial manufacturing processes. Fewer by-products (or less toxic by-products) will lead to financial as well as environmental benefit. However, if waste must be generated, where possible, it should be put to good use. For example, bottles may be re-filled and tyres may be re-treaded. If waste cannot be economically re-used, it should be exploited for its material value, through recycling, composting or incineration with energy recovery. Finally, as a last resort, waste that cannot be dealt with in one of the previous manners should be disposed of in the most environmentally friendly way practicable, with hazardous materials being rendered harmless. Incineration (without energy recovery), or landfill constitute ultimate waste disposal routes. In the UK, no municipal solid waste (MSW) is now incinerated without energy recovery (DEFRA, 2005a).

In this context, about 9% of UK controlled waste is incinerated, at one of 12 Municipal Solid Waste (MSW) incinerators (DEFRA, 2005a, Environment Agency, 2005). The incineration process reduces the residual amount of waste (as ash) to about 10% of original volume, and 30% of original mass. Energy can be recovered from incinerated material, through electricity generation, or district heating schemes. This processing of the waste therefore has benefits in minimising the amount of waste material remaining, and gaining some energy value from the waste material. Nevertheless, the process is publicly unpopular, due to concerns over pollution, both from the solid residues which remain, and particularly over atmospheric pollution arising from the process, and thus incineration is often seen as an environmentally unacceptable form of waste management (Kirby, 2001).

Much of the public opposition appears to be based on the historic reality of incinerators, which were poorly controlled and hence highly polluting. There were significant atmospheric emissions of particulates, sulphur dioxide, hydrogen chloride, heavy metals and partial combustion products, including dioxins. As such, in the past incinerators have had a negative impact both on the environment and human health.

However, as environmental awareness and regulatory burden grew, pre-release clean-up of gas streams became an integral part of the incineration process. Much has been learnt about the combustion process, formation of pollutants and pollutant removal, and there have been significant technological improvements to the process. Initially, water sprays, cyclones and electrostatic precipitators were used to remove particulate matter (Greenberg et al., 1978), though these have now been superseded by complex scrubbers and bag filters, which remove many pollutants, notably particulates, acidic and corrosive gases, heavy metals, and organic products of incomplete combustion (Hester and Harrison, 1994). Thus MSW incineration is now a highly sophisticated and relatively "clean" waste processing system (Figure 1).

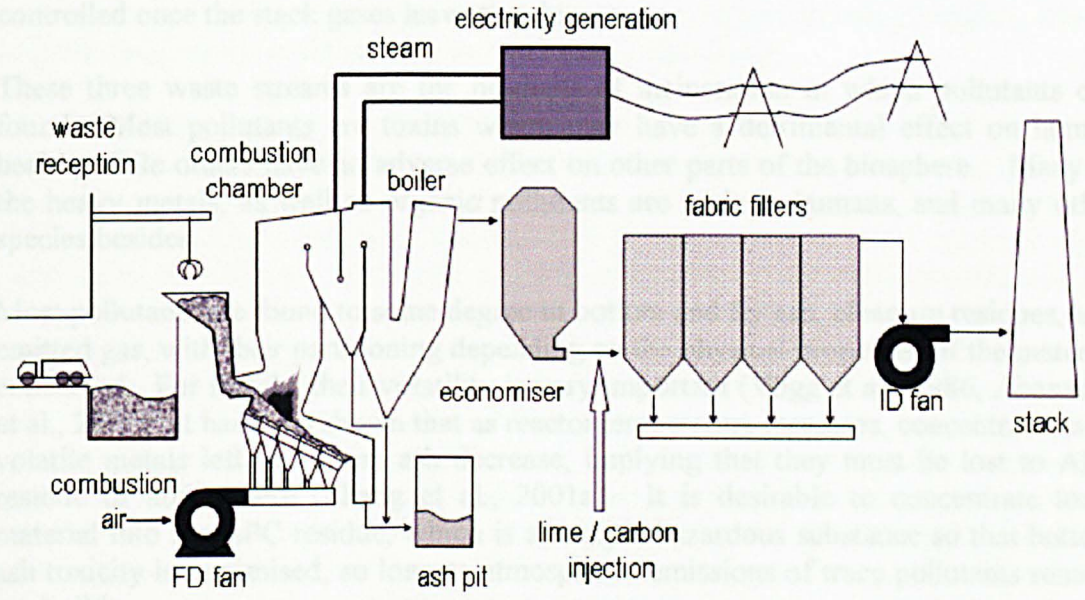


Figure 1: The layout of a typical MSW incineration plant

However, though the MSW incineration process has improved substantially over recent years, the process is still not perfect. Two types of solid waste still arise from incineration; bottom ash, which is removed from the end of the furnace bed, and Air Pollution Control (APC) residues which arise from flue gas clean-up. Liquid wastes may arise from flue gas cleaning (wet scrubbers), and there are gaseous emissions to the atmosphere. Such products of incineration must be taken into account when considering the relative merits of this waste treatment option (Williams, 1990). Legislative restrictions on atmospheric pollutant emission from incineration are rigorous, and solid residues are also tightly controlled. The EC waste incineration directive [2000/76/EC], adopted by England and Wales, and replacing earlier legislation [89/369/EC and 89/429/EC], limits the concentrations of certain species in products from incineration (European Community Legislation, 2000a, European Union, 2005).

Thus it is seen that although incineration is not perfect waste management technology, it can have its part to play in a wider waste management strategy, if carefully controlled. In terms of current UK policy, it is not a question of whether or not to use incineration for waste management, but how to optimise and increase its use, as it is seen as one of the better waste management techniques for waste which cannot be recycled (DEFRA, 2000, DEFRA, 2005a, DEFRA, 2005b). In order that incineration is therefore safe, and hopefully publicly acceptable, it must be ensured that emissions

limits are consistently met, and further research must be conducted, in a continual effort towards optimising the waste incineration process.

1.1.2 Pollutants from MSW Incineration

Although the legislation tightly limits air emissions from incineration, it is pollutants in the stack gas (the majority of which is carbon dioxide and water) which generally cause the most public concern (Williams, 2005). Usually, bottom ash is land-filled, as are APC residues (though its composition means that it must be disposed of as hazardous waste, due to the heavy metal and trace organic contaminants). Whereas these solid residues may be reliably localised and immobilised (for many years at least), airborne contamination is of greater concern, as their distribution cannot be controlled once the stack gases leave the chimney.

These three waste streams are the products of incineration in which pollutants can found. Most pollutants are toxins which may have a detrimental effect on human health, while others have an adverse effect on other parts of the biosphere. Many of the heavy metals, as well as organic pollutants are toxic to humans, and many other species besides.

Most pollutants are found to some degree in bottom and fly ash, clean-up residues, and emitted gas, with their partitioning depending on the physical properties of the material concerned. For metals, their volatility is very important (Vogg et al., 1986, Abanades et al., 2001). It has been shown that as reactor temperature increases, concentrations of volatile metals left in bottom ash decrease, implying that they must be lost to APC residue or atmosphere (Zhang et al., 2001a). It is desirable to concentrate toxic material into the APC residue, which is already a hazardous substance so that bottom ash toxicity is minimised, so long as atmospheric emissions of trace pollutants remain negligible.

Organic pollutants arising from incineration have two likely sources; either they were present in the incinerator feed and were not destroyed, or they were formed from products of incomplete combustion (PICs) during the incineration process. Organic pollutants are typically highly stable species, with long half-lives in the environment. Examples include Polyaromatic Hydrocarbons (PAHs), PolyChlorinated Biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs). These families of organic compounds encompass a large number of specific molecules, each of which has different toxicities.

While it may be possible to remove organic pollutants from the gas stream, a more preferable approach is to prevent their re-formation, through careful control of incinerator conditions. Following extensive research, it is known that burner and flue temperature, gas composition, redox environment and the presence of species, which may catalyse reactions (i.e. particulates) are all factors known to influence organic pollutant production, and incinerator design and operation specifications are designed to ensure (as far as possible) complete burn-out of organic pollutants (Williams, 1998, European Community Legislation, 2000a). Nevertheless, some production of organic pollutants is unavoidable, and the gas clean-up, which usually includes activated carbon injection to absorb organic pollutants, ensures that the stack gas concentrations are acceptable.

The main inorganic pollutants of concern are metals and metalloids, notably heavy metals such as cadmium, lead, and mercury. Volatile metal species tend to be found largely as small (<10μm) particulates (PM_{10}) in the stack gas, though these are largely removed by the air pollution control devices. Less volatile metals are found in the bottom ash. Unlike organic pollutants, metals which are present in the incinerator feed must ultimately be present in the incinerator output, either in gaseous emissions or solid residue, as elementally they cannot be destroyed. Therefore, the aim in control of these components must be subtly different from those for organic pollutants. If the metals cannot be removed from the feed (often the most desirable solution), their effect in the incinerator output must be minimised. Presence as particulates in emitted flue gas is seen as highly undesirable, as their distribution cannot then be controlled, and such small particles can become trapped in the lungs, where the physiological effects of toxic metal compounds tends to be particularly significant.

1.1.3 The Behaviour of Metals in MSW Incineration

Ever since metal partitioning in an incinerator was investigated in detail, there has been a great deal of interest in how metals behave in incineration conditions (Brunner and Monch, 1986, Linak and Wendt, 1993). Nevertheless, information on the partitioning of different metals between different residues, and the processes causing transportation, is limited, and so precise control of metal distribution is not really practical: indeed data on metals in incineration is extremely limited (Lockwood and Yousif, 2000, Morf et al., 2000, Linak and Wendt, 1993). Analysis is made more complex by the variability and lack of homogeneity of the residues, which can make sampling errors highly significant (Reimann, 1989). The data on gaseous emissions is even more limited, with traditional analysis techniques only allowing average values to be obtained, and with legislative drivers only requiring the measurement of specific metals, and at relatively infrequent intervals. New data on the presence of volatile toxic metals in incineration, their behaviour, and their variation with time would be highly useful for an improved understanding of the processes involved, which should lead to improved incinerator operation.

Nevertheless, key variables have been identified which are important in determining metal partitioning:

- The nature of the incoming waste – its physical and chemical nature.
- The physical and chemical properties of the metal of interest
- The physical and chemical environment in the furnace.
- The physical and chemical properties of the flue gas treatment system.

Inert (non-combustible, non-volatile) solids remain on the grate, and exit the incinerator in the bottom or grate ash. For most metals, we may think of this as the "default", unless some active process occurs to cause its removal from the burning bed. If the metal (in any chemical form) is to leave the burning bed other than in the bottom ash, it must be via the raw flue gases. An active transport process must occur to transport the metal with the flue gases, and two possible mechanisms exist. For volatile metals, the heating of the metal in the furnace may cause it to **volatilise**, and the vapour will be transported through the incinerator along with other gaseous combustion products. Alternatively, for non-volatile metals, small solid particulates containing the metal may be **entrained** in the gas stream (Linak and Wendt, 1993, Belevi and Moench, 2000a). Thus volatilisation and entrainment are the two most

important processes in metal transport in incinerators, and anything which affects these processes is therefore of interest.

Mathematical modelling techniques have been used to predict where the metals entering the incinerator leave the incinerator, either in the bottom ash, APC residue, or flue gas, and to try to understand the transport phenomena involved. Having seen how important metals are, in terms of the incineration process and its environmental impact, it should be clear why an improved theoretical understanding of how metals behave in such systems is so important. Following initial experimental investigations of metal partitioning, many studies have attempted to model the behaviour of metals in incinerators and other combustion systems, with varying degrees of success, and using different modelling techniques (Brunner and Monch, 1986, Linak and Wendt, 1993, Barton et al., 1990, Lockwood and Yousif, 2000).

In thermodynamic equilibrium modelling, it is assumed that all the components in the fuel are exposed to the conditions found in the combustion system, and reach full thermodynamic equilibrium with one another, yielding solid, liquid, and vapour products (Delay et al., 2001, Wu and Biswas, 1993). Both pure species and mixtures (slags and melts) may be obtained. The volatility of different products determines which species leaves the furnace as a vapour (which is captured in the APC device, or emitted with stack gas), or are retained in the solid (bottom ash). These studies not only give indications of the species which are important in metal transport, but can also indicate which system variables (e.g. plant temperature, chlorine concentration in waste) may have a significant effect on metal distribution (Wu et al., 1994). However, if models are solely thermodynamic in nature, they cannot account for entrainment, which is also important in metal transport.

Although the previous work on thermodynamic prediction of metal partitioning is generally excellent, it also demonstrates well the difficulties generally encountered with the technique. Firstly, there is an incomplete availability of data on the thermodynamics of all the reactions which may be significant. The situation has improved, and there are now a number of very comprehensive databases of thermodynamic information that may be used by modelling packages. Secondly, a more fundamental issue is whether it is reasonable to assume a global thermodynamic equilibrium for a combustion system, where waste input and combustion parameters change substantially over time, and may vary significantly within the incinerator, at a given time.

Ideally, the aim of modelling metal behaviour in a combustion system would be to produce a fully descriptive kinetic model, of how and why any metal behaves the way it does in the system. However, the input data requirements (in terms of the waste input, and the combustion process), would be extremely significant, and any results would be highly specific to a particular plant working under specific conditions, and such an objective is not realistic at this time. A major problem of increasing model complexity is the data availability, especially if it is to account for variation in a process as inhomogeneous as MSW incineration. Information on the waste feed, or the nature of the combustion on the burning bed, is simply not known to the required accuracy. Even if it were, such values would be subject to change (with combustion conditions) to a degree where the modelled results would vary unacceptably, given the range of conditions which may normally be encountered. Thus the need for improved

modelling techniques is always balanced by the need for better information on the incineration process on which the model can be founded.

The verification of the accuracy of computed models can also be a problem. This is especially true for MSW incineration, where the input waste is particularly poorly characterised. In contrast, models for coal or hazardous waste incineration, where the input composition is better known, have been more verifiable (Linak and Wendt, 1993, Delay et al., 2001). For a waste stream as diverse and inhomogeneous as municipal waste, it is doubtful whether any model could ever be fully quantitative and fully predictive of residue compositions. Nevertheless, the models which are available allow us to gain an improved understanding of how physical and chemical parameters determine metal partitioning, and investigate theoretically how changing processes can change metal behaviour.

Thus it is seen that although considerable efforts have already been made to model behaviour in combustion systems, including MSW incineration, there is also room for substantial improvement, in order to improve our overall understanding of the fundamental principles involved. However, there are inherent limitations to the viability of computational modelling of such complex "real systems", and such models must always be supported by comprehensive experimental data.

1.1.4 Measurement of Metallic Pollutants in MSW Incineration

Emissions monitoring is conducted for three main reasons; to ensure that legislative requirements are being met, to optimise process to minimise emissions, and to demonstrate to the public that a process is being run in an environmentally responsible manner possible (Scott, 1995, Meyer, 1995). Having established that the products from a process such as incineration require measurement, appropriate analytical techniques must be developed, as well as safe limits being set.

As the fate of metals in incineration is of technical and environmental importance, there is a need to identify the presence and partitioning characteristics of metallic species found in different incineration products. It is therefore essential to have adequate analytical techniques, for the relevant metals, in bottom ash and APC residue, any process water produced, and the emitted flue gas, to determine which metals are present, and at what concentration. It is also desirable to know how concentrations vary with time, and what degree of homogeneity is observed in the samples taken.

As with any other, the field of environmental analytical chemistry is constantly developing. As analytical and electronic technology improves, detection limits improve, analysis times are reduced, instrument cost and size are reduced, and resolution is improved. However, as well as these continual improvements, a step-change in analytical requirements is being observed. Historically, samples would be collected of a material of interest, such as an ash, soil, or process water, and would be returned to the laboratory for analysis. As technology has improved, environmental awareness grown, and legislative requirements become more rigorous, there has been a move towards the requirement for **Continuous, On-line, automated analysis** of process products.

Continuous monitoring is preferable, in that it allows real-time data acquisition (which may be linked to feedback control systems). Such data can be directly related to current process conditions, and specific problems or optimisations can be identified.

Thus it can immediately be seen if there is a problem in a process, and as such if emissions are above set limits. In this case, corrective action can immediately be taken, provided that results are available rapidly enough. This is in contrast to traditional discrete sampling, where the results may take days or weeks to arrive, and when they do, they are time-averaged for the length of the monitoring period (as determined by the size of the sample collected). If the emissions are excessive or the product unsatisfactory, it is too late to alter the process, and modifications or improvement can only be made retrospectively. However, the advantages of on-line monitoring are accompanied by increased equipment complexity and cost, if indeed such equipment is available.

It is not currently possible to continuously monitor the vast number of possible organic and inorganic emissions from incinerator stacks, and so periodically, discrete samples are analysed for dioxin and metal content. O_2, CO, NO_X, SO_2, HF, and HCl are monitored continuously, along with incinerator temperature, to ensure thorough and clean combustion, and thus legislative compliance.

Although continuous monitoring of metals and metalloids in incinerator flue gas is not yet required, it is to be expected that such monitoring will one day become mandatory, with current EC legislation indicating that the introduction of such measurement techniques is expected when the technology becomes available. This legislation is next due for review in 2008 (European Community Legislation, 2000a). There is therefore currently significant research interest in new continuous emissions monitoring technologies for metals.

If metal emissions in incinerator residues were also to be measured continuously, these would provide extra information for the regulators, and also secondary information on plant operation, which would allow process optimisation. Sampling after the APC device would indicate stack emissions, and pre-APC device measurement would give measurements which were indicative of the composition of APC residues. There would seem to be little interest in continuous measurement of bottom ash composition, which is probably technically near-impossible, given its inhomogeneity, and difficulties associated with obtaining representative samples as a result (Reimann, 1989).

With modern analytical instrumentation, continuous monitoring of some sample streams may be quite straightforward, following relatively minor modifications to the sample introduction system for on-line analysis. As conventional discrete samples may require extensive preparation before analysis (particularly inhomogeneous solids), which is time consuming and hence costly, alternative sample introduction techniques, including continuous monitoring systems are desirable, if the capital costs can be met (Ward, 1995). A liquid sample can be pumped from the process to the analyser, and provided that extensive pre-treatment is not required, can be introduced as a standard liquid sample, with the instrument set to take multiple measurements (Spectro, 2005). Even homogeneous solids, such as steel samples, can be analysed in a completely automated manner (Kamphoff, 2004). Gaseous samples can be introduced continuously to a plasma, or indeed a plasma can be generated inside a duct carrying a gas. For relatively clean and stable gas streams, accurate, sensitive monitoring of metals in gases has already been achieved (Klinkenberg et al., 1997), but the application of continuous monitoring techniques to the relatively difficult matrix of flue gas is still in the developmental stage.

1.1.5 Summary

Thus it is seen that although a great deal is already known about the incineration of waste, and in particular the behaviour of metals, our understanding of the processes involved is still limited, particularly with respect to the effects of temporal changes in waste feed and combustion conditions on metal partitioning. The lack of temporally resolved data particularly limits further advances in knowledge, and both improved experimental data, and mathematical modelling techniques could help to advance the state-of-the-knowledge for these environmentally significant constituents of normal municipal solid waste.

1.2 Research Objectives

The overall objective of this research is to develop a comprehensive understanding of the behaviour and distribution of metals during MSW incineration, including an assessment of the importance and effect of temporal variations in waste composition and incineration conditions, through experimental measurement, and mathematical modelling. In order to achieve this, the following sub-objectives must be addressed:

- Review the current knowledge, as presented in the literature, relevant to this study. This will include information on municipal waste, its incineration (with particular reference to the behaviour of metals), the relative technical and toxicological importance of different metals, analytical techniques for these metals in combustion systems, and available techniques for predicting/modelling the behaviour of these metals.
- Develop tools for the measurement of metal concentrations in incinerator residues. In particular, develop techniques for the continuous, on-line monitoring of metal concentrations in flue gases.
- Develop improved theories of how metals behave during MSW incineration. In particular, there is a need to develop techniques which account for temporal variations in waste feed and combustion conditions.
- Compare predicted and experimental results, using experimental data obtained in the formation of the models, and in validating the theoretical answers obtained.
- Review and assess the theoretical and experimental data to obtained, to assess its agreement, and see how this contributes to knowledge of the behaviour of metals in municipal solid waste incineration.

The first objective, to review the literature relevant to this study, is the subject of the following chapter.

Chapter Two:

Literature Review

This chapter reviews existing literature relevant to this research. The problem presented by municipal waste is discussed, and the role of incineration in waste management is examined. Specific issues regarding the behaviour and effects of toxic metals in incineration are discussed in detail, and methods of analysis for these species are reviewed. The importance of continuous monitoring in incineration is identified, given that such processes change over time. Computational methods of rationalising the behaviour of metals in combustion systems are investigated. Through the review of existing work, key objectives for this research are identified.

2.1 Municipal Solid Waste and Incineration

2.1.1 The Problem of Waste

The management of waste, from its generation to its ultimate disposal, is a difficult and controversial practical and political problem. None of the available options are ideal when considering how do cope with the 250 million tonnes of controlled (Household, Commercial and Industrial) waste produced in the UK every year (Williams, 1998), and the question of how best to deal with this material is one which must be addressed (Hester and Harrison, 1994).

Traditionally, the main disposal route for waste in the UK has been landfill. In 1996, 90% of waste was landfilled. However, it has been recognised that this disposal route is not sustainable, and by 2000, the proportion had dropped to 78%. The availability of space, not to mention new resources, means that new methods of waste disposal, including reduction of production, must be found. Difficult, subjective and possibly publicly unpopular decisions must be made.

Despite this, the amount of waste being generated is not decreasing significantly. Between 2001 and 2004, the amount of municipal waste generated has remained approximately steady at about 29 million tonnes (DEFRA, 2005b). In this context, if the amount of material reaching landfill is to decrease, other waste management strategies must be found. Consequently, there has been a governmental drive to increase recycling and composting, and as a result, the proportion of municipal waste being recycled or composted has risen consistently in recent years as shown in Table 1 (DEFRA, 2005a, DEFRA, 2005b). Another alternative is the incineration of waste, which reduces its mass and volume, while providing energy from the heat generated by the process. However, this option is publicly unpopular, due to concerns over pollution, both from the solid residues which remain, and particularly over atmospheric pollution arising from the process (Kirby, 2001). Despite of this, about 9% of UK controlled waste was incinerated in 2003-4, and this proportion is set to increase under current government recommendations (DEFRA, 2005a, DEFRA, 2005b).

Table 1: Municipal waste disposal routes (DEFRA, 2005a, DEFRA, 2005b)

year	municipal waste arising (M tonnes)	proportion landfilled (%)	proportion recycled or composted (%)	proportion incinerated (with energy recovery) (%)
2001-2	28.9	78	14	8
2002-3	29.4	75	16	9
2003-4	29.1	72	19	9

In making decisions about how to handle waste, different environmental factors may compete with each other when considering the best waste management option for a particular waste stream. For example, Nickel-Cadmium batteries pose a significant environmental risk due to their cadmium content, and ideally none would be incinerated or land-filled, and in these terms a recycling rate of 100% is ideal. However, this must be balanced with increasing collection, transport and management costs for recycling, as the proportion recycled increases, with the collection system having a significant environmental impact itself (Rydh and Karlstrom, 2002). It is therefore not always easy to decide on the best overall waste management strategy.

2.1.2 The Composition of Municipal Waste

One of the first problems encountered in managing waste is identifying the composition of the waste, as this affects how it may best be handled. Due to the extremely heterogeneous nature of waste, characterising the material is extremely difficult, as it is almost impossible to be sure that the waste sampled is representative of the whole waste stream it comes from. Thus large studies are required to accurately analyse the composition of waste, either in terms of the components in the waste, or its elemental analysis (Reimann, 1989, Van Der Sloot et al., 1997, National Assembly for Wales, 2004, Morf and Brunner, 1998). Figure 2 and Figure 3 illustrate two different analyses of the composition of municipal waste, giving some indication of the typical material being handled.

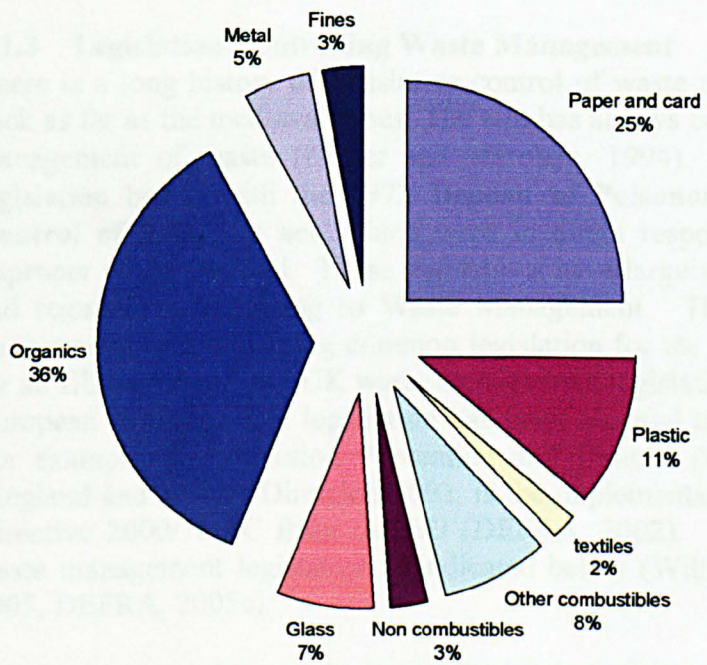


Figure 2: The composition of municipal waste by material (National Assembly for Wales, 2004)

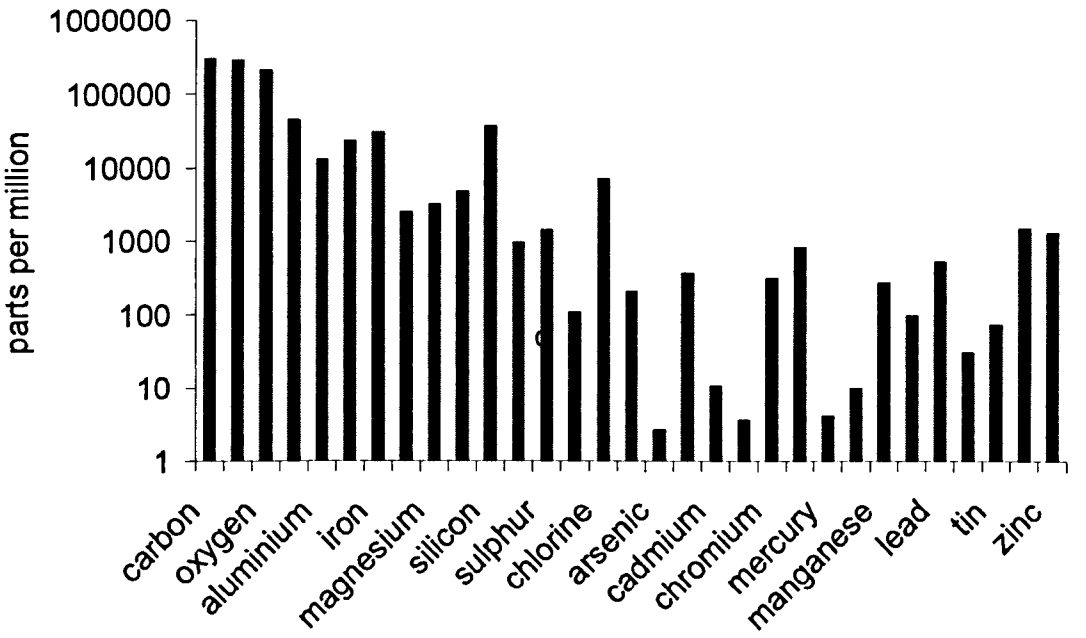


Figure 3: The elemental composition of municipal waste (Belevi and Moench, 2000b)

The highly varied composition of waste makes its management especially difficult. The majority of the mass is relatively non-toxic and non-problematic (carbon, oxygen, aluminium, iron, silicon magnesium etc). However, within the waste there are also far more toxic species (e.g. lead, cadmium, mercury), and potentially pathogenic species. These may be distributed in a dilute form in large volumes of waste, or may be concentrated in specific items. All these factors make waste potentially hazardous, and mean that it must be managed appropriately, and the first step towards this is knowing as accurately as possible what the waste is comprised of.

2.1.3 Legislation Controlling Waste Management

There is a long history of legislative control of waste management in the UK, going back as far as the medieval times. The aim has always been to ensure safe, responsible management of waste (Hester and Harrison, 1994). Modern waste management legislation began with the **1972 Deposit of Poisonous Waste act**, and the **1974 Control of Pollution act**, which were in direct response to a number of cases of improper waste disposal. These regulations have largely been superseded by new acts and regulations pertaining to Waste Management. The European Union has been instrumental in establishing common legislation for the control of waste management for all EU members, and UK waste management legislation is largely part of this wider European strategy. UK legislation has been adopted to enforce such EU directives. For example, the Pollution Prevention and Control (Waste Incineration Directive) (England and Wales) Direction 2002, is the implementation of the Waste Incineration Directive 2000/76/EC from the EU (DEFRA, 2002). Key historic and current UK waste management legislation is indicated below (Williams, 1990, European Union, 2005, DEFRA, 2005c):

The Environmental Protection Act 1990. Part I: Integrated Pollution Control and Air Pollution Control by Local Authorities.
The Environmental Protection Act 1990 Part II: Waste on Land.

The Environmental Protection (Prescribed Processes and Substances) Regulations 1991 (and subsequent amended regulations)
The Environment Act 1995
Pollution Prevention and Control Regulations 2000
(Including Pollution Prevention and Control (Waste Incineration Directive) (England and Wales) Direction 2002)

There are also many regulations controlling specific waste management techniques, or waste streams, for example regulations on the proper management of waste electrical and electronic equipment (European Community Legislation, 2002a), and on the control of municipal waste incinerators (European Community Legislation, 2000a).

Rather than attempt to describe every piece of waste management legislation in detail, the underlying principles of the legislation as a whole will be described. As such, the following section summarises important aspects of the legislation relating to waste management as the law as a whole now stands.

The Hierarchy of Waste Management
The current fundamental strategy adopted throughout the EU and beyond is the **hierarchy of waste management**. This strategy seeks to deal with waste in the best manner, with the order of preference being **reduction**, **re-use**, **recovery** or **disposal** (Williams, 1998):

The best way to deal with waste is to minimise its production, through improved, higher efficiency industrial manufacturing processes. Less by-products (or less toxic by-products) through improved process, will lead to financial as well as environmental benefit. Retailers and Consumers can participate in waste reduction, for example by reducing use of un-necessary packaging. In recent years, manufacturers have been able to reduce the amount of materials used, for example for packaging, through improved processing (e.g. the ability to create thinner metal sheet for food cans), so reducing waste production (Williams, 2005).

However, if waste must be generated, where possible, it should be put to good use. For example, bottles may be re-filled, tyres may be re-treaded, and redundant items may be transferred to another user. In doing so, care must be taken to ensure that the energy costs (e.g. of transportation and cleaning) do not outweigh the benefits of re-use. Therefore, if waste cannot be economically re-used, it should be exploited for its material value, through recycling, composting or energy recovery. For example, glass, ferrous, and non ferrous metals can be separated and recycled, garden waste can be composted, and combustible material can be incinerated to generate energy, through district or process heating, or electricity generation. However, there is a legal distinction between material recovery (e.g. composting and recycling) and incineration for energy recovery, with material recovery techniques being preferred (Coggins, 2003).

Finally, as a last resort, waste that cannot be dealt with in one of the previous manners should be disposed of in the most environmentally friendly way practicable, with hazardous materials being rendered harmless. Incineration (without energy recovery), or landfill constitute ultimate waste disposal routes. In the UK, no MSW is now incinerated without energy recovery (DEFRA, 2005a).

Definition and Quantification of Waste

One of the problems encountered when considering waste management options is the lack of good, comparable data on waste arisings, disposal routes, and composition. It can then be difficult to compare different waste management techniques due to different measures used to analyse the detrimental effects of those processes. Precise legal definitions of different wastes may affect how governments consider its management. Different authorities may interpret these definitions differently, and different countries tend to use different definitions. This all makes direct comparison of data extremely difficult, and as a result, EU legislation has sought to define waste better, and the EU has commissioned studies to ensure the better characterisation of waste arising (DEFRA, 2005a, Williams, 2005, O'Connell, 2002, European Community Legislation, 2000c).

Household, commercial and industrial wastes are classified as Controlled Wastes. Mine, quarry and agricultural wastes are uncontrolled. Controlled wastes include sewage sludge, and medical waste, which require special treatment or disposal. Certain wastes are classified as Special or Hazardous, if they are dangerous or difficult to keep, treat, or dispose of. They are defined as containing substances that are dangerous to life [or by implication to the environment] (Williams, 2005). The focus of this work is on municipal waste.

Responsibility for Waste Management

The aim of modern legislation has been to make the original producer of waste responsible for its management. The producer is obliged to ensure its safe management, from production to eventual disposal (Williams, 2005, European Community Legislation, 2000b, European Community Legislation, 2002a).

Waste Management Strategy and Environmental Impact Assessment

Two principles govern environmental considerations of waste management, Best Practicable Environmental Option (BPEO), and Best Available Techniques Not Entailing Excessive Cost (BATNEEC). These are determined for any proposed prescribed waste management operation by completion of an environmental impact assessment (EA). When gaining approval for a waste management technique, operators must show that the process meets the requirements of BPEO, and this will mean that emissions to air, water, or soil, must be at or below levels laid down in a number of legislative acts, and may be subject to further local restriction (Williams, 2005).

National, regional and local governments must have in place strategies for waste management. Strategies must be in agreement with the waste management hierarchy, and must address waste collection, recycling, and disposal. Individual waste treatment facilities must be viewed with respect to the overall plan, which should be in agreement with the principles of Integrated Pollution Control (IPC), which is now administered by the Environment Agency. As well as satisfying the Environment Agency requirements, waste management facilities must satisfy the demands of the Town and Country Planning Acts.

There is an inherent problem that most people see waste management as an undesirable process, whichever options are adopted. This leads to problems of the attitude of "Not In My Back Yard" (NIMBY), meaning that local authorities are under considerable pressure not to allow waste management facilities in their areas. As waste must be

dealt with somewhere, the "proximity principle" is applied, meaning that waste should be dealt with as close as possible to its origin. Local Authority waste management plans should assess the need for waste management, and as far as possible, seek to deal with waste within the area (Williams, 2005).

Waste Legislation Outside the EU

In many cases, developments in US Laws, Statutes and Regulations approximately parallel UK and European legislation. Early laws prohibited indiscriminate dumping of rubbish. Modern regulations began to appear in the 1970's, when the problems arising because of inappropriate waste disposal became apparent (Hester and Harrison, 1994). It is intended that further legislation will be introduced as required, to further regulate the industry and minimise environmental effects of waste management. Ultimately, it is the Environmental Protection Agency (EPA), a federal government agency, determines environmental requirements for waste treatment and disposal facilities. However, state and local governments have responsibilities for administration of policy, and may elect to require standards higher than the national minimum.

Regulations outside the EU and US are many and varied, with waste management standards in less developed countries being far lower. In many cases, practices which were considered unacceptable more than 20 years ago in the UK are still commonplace in other parts of the world, particularly with respect to waste incineration. In this context, it is important to remember that internationally, vast improvements are still required to the way in which waste is managed (Russel and Vogel, 2003). Further technological and political effort is still required before the best strategies for waste management are applied and enforced internationally (Williams, 2005).

2.1.4 Incineration of Waste as Part of Waste Management

About 9% of UK controlled waste is incinerated (DEFRA, 2005a). The incineration process reduces the residual amount of waste (as ash) to about 10% of original volume, and 30% of original mass. This processing of the waste therefore has benefits in minimising the amount of waste material remaining, but the process is not perfect. Two types of solid waste arise from incineration; bottom ash, which is removed from the end of the furnace bed, and Air Pollution Control (APC) residues (including fly ash), which arise from flue gas clean-up. Liquid wastes may arise from flue gas cleaning (wet scrubbers), and there are gaseous emissions to the atmosphere. Such products of incineration must be taken into account when considering the relative merits of this waste treatment option (Williams, 1990).

Energy can be recovered from incinerated material, through electricity generation, or district heating schemes. In this context, waste has been seen as a renewable energy source, contributing to the electricity generation Non Fossil Fuel Obligation (NFFO). However, recent European court rulings have challenged this classification, making it likely that in the future, this premium will not be available for electricity generated by waste incineration (Coggins, 2003).

Despite the advantages outlined above, incineration is often seen as an undesirable and environmentally unacceptable form of waste management. Much of the opposition appears to be based on the historic reality of incinerators, which were poorly controlled and hence highly polluting. There were significant atmospheric emissions of both heavy metals and partial combustion products, including dioxins, and as such

incinerators have had a negative impact both on the environment and human health. However, much is now known about the combustion process, formation of pollutants and pollutant removal, and significant technological improvements to the process mean that incineration plants now provide a highly sophisticated and relatively "clean" waste processing system (Figure 4).

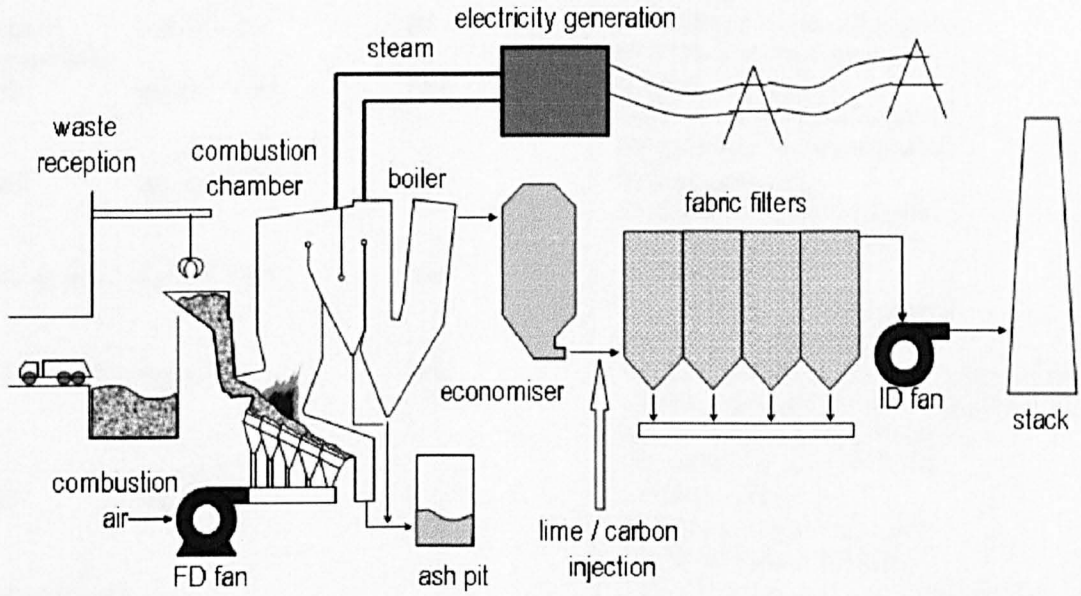


Figure 4: The layout of a typical incineration plant

In addition, judicious use of incineration as part of a wider waste strategy, with careful pre-sorting of rubbish, may significantly improve its environmental acceptability. For example, targeted removal of particular waste streams, (e.g. Nickel-Cadmium batteries) could have significant effects on metal outputs from incineration (Rydh and Karlstrom, 2002, Vogg et al., 1986).

Thus it is seen that although incineration is not perfect waste management technology, it can have its part to play, and this is optimised by its careful use as part of a wider waste management strategy. In terms of current UK waste management strategy, it is not a question of whether or not to use incineration for waste management, but how to optimise its use, as it is seen as one of the better waste management techniques for waste which cannot be recycled (DEFRA, 2000). In order that incineration is therefore safe, and hopefully publicly acceptable, it must be ensured that emissions limits are consistently met, and further research must be conducted, in a continual effort towards optimising the waste incineration process.

2.1.5 Legislation Controlling Incineration in the UK

Legislative restrictions on atmospheric pollutant emission from incineration are rigorous (Table 2), and solid residues are also tightly controlled. Nevertheless incineration is still publicly unpopular, with atmospheric emissions (which are inherently widely distributed) causing the most concern. The EC waste incineration directive [2000/76/EC], adopted by England and Wales, and replacing earlier legislation [89/369/EC and 89/429/EC], limits the concentrations of certain species in products from incineration, within the context of the EU waste legislation framework (European Community Legislation, 2000a, European Union, 2005).

Table 2: Incinerator gaseous pollutant concentration limits under different legislation

emission parameter	units	EU 1989/369/EC (new plant)	UK IPR 5/3	EU 2000/76/EC (all plant)
particulate	mg m^{-3}	30	30	10 (daily average) 30 (100% of ½ hour averages) 10 (97% of ½ hour averages)
organic compounds	mg m^{-3}	20	20	20 (100% of ½ hour averages) 10 (97% of ½ hour averages)
CO	mg m^{-3}	100	100	50 (daily average) 150 (95% of 10 min averages) 100 (100% of ½ hour averages)
HCl	mg m^{-3}	50	30	10 (daily average) 60 (100% of ½ hour averages) 10 (97% of ½ hour averages)
SO_x as SO_2	mg m^{-3}	300	300	50 (daily average) 200 (100% of ½ hour averages) 50 (97% of ½ hour averages)
NO_x as NO_2	mg m^{-3}	-	350	200 (daily average, new plant, and existing > 6t/hour with staged implementation) 400 (100% of ½ hour averages) 200 (97% of ½ hour averages)
HF	mg m^{-3}	2	2	1 (daily average) 4 (100% of ½ hour averages) 2 (97% of ½ hour averages)
heavy metals:				Average values over the sample period (30 minutes - 8 hours)
class I Hg	mg m^{-3}	0.2	0.1	0.05 (new plant) 0.1 (existing plant until 2007)
Cd	mg m^{-3}	0.2	0.1	0.05 (new plant – sum of Cd +Tl) 0.1 (existing plant until 2007 – sum of Cd+Tl)
class II As, Co, Se, Ni	mg m^{-3}	1	1	sum of Class II and III metals, not including Se and Zn (now no longer regulated, also including Sb, Mn and V. 0.5 (new plant) 1.0 (existing plant until 2007)
class III Pb, Cr, Cu, Zn	mg m^{-3}	5	1	
dioxins TEQ	ng m^{-3}	-	1 (target 0.1)	0.1 (average value over the sample period of 6 to 8 hours)
reference period		month	day	as detailed
Reference conditions		101 kPa, 11% O_2, dry gas	101 kPa, 11% O_2, dry gas	101 kPa, 11% O2, dry gas

A second piece of legislation which has had significant impact on the role of incineration in waste management is the landfill tax directive. This tax, on waste which is land-filled, has helped to redress a cost imbalance between landfill and other waste treatments such as incineration, which have traditionally been significantly more expensive (Table 3). This tax was introduced in 1996, and increases annually (Table 4), thus increasing the economic viability of incineration as a waste treatment option. The intention is to continue annual increases in the rate of this tax to a "medium to long term rate of £35 per tonne" (H M Revenue & Customs, 2005a).

Table 3: Estimated cost of waste disposal in the UK by different means (Williams, 2005)

disposal route	estimated cost per tonne [1]
incineration (100 000 T/annum plant with energy recovery)	£47
incineration (200 000 T/annum plant with energy recovery)	£31
landfill (175 000 T/annum site with energy recovery)	£19 cost + £18 tax = £37[2]

[1] assuming a currency conversion rate of 1 Euro = 68 pence
[2] after 1st April 2005

Table 4: The landfill tax levy (H M Revenue & Customs, 2005a, H M Revenue & Customs, 2005b)

effective date	end date	tax cost per tonne
01 10 96	31 03 99	£7
01 04 99	31 03 00	£10
01 04 00	31 03 01	£11
01 04 01	31 03 02	£12
01 04 02	31 03 03	£13
01 04 03	31 03 04	£14
010404	310305	£15
010405	310306	£18

Thus it is seen that the legislative framework in which incineration takes place is rigorous, and controls on the process are stringent. Nevertheless, incineration for waste management remains unpopular, due to perceptions of damage caused by incineration. The following sections will examine what pollutants are significant during incineration, and how their effect can be minimised.

2.1.6 Environmental Concerns Arising from Incinerators

Figure 4 is a schematic diagram of the incineration process, and from it can be seen all of the products (desirable and otherwise) which arise from the process. Using an input of waste alone, electricity is produced, along with bottom ash (which is relatively inert), air pollution control (APC) residue (collected by the bag filters and boiler, and significantly hazardous), and stack gas. Although the legislation tightly limits air emissions from incineration, it is pollutants in the stack gas (the majority of which is carbon dioxide and water) which generally cause the most public concern (Williams, 2005).

These are the products of incineration in which pollutants can be found. Typical heavy metal and dioxin concentrations in these residues are shown in Table 5. Many of the heavy metals, as well as organic pollutants are toxic to humans, and many other species besides. The physical and chemical form in which the pollutant leaves the incinerator is significant, as it affects its distribution in the environment, and thus the exposure route to susceptible targets. This is why airborne contamination is of such concern, as its distribution cannot be controlled, whereas solid residues may be more reliably localised and immobilised, for many years at least.

Table 5: Typical concentrations of different pollutants found in incinerator residues

species	concentration in bottom ash (mg Kg^{-1})	concentration in fly ash (mg Kg^{-1})	concentration in stack gas ($\mu g\ m^{-3}$)
arsenic [1]	10 - 80	40 - 120	<50
cadmium [1]	0.5 – 10	50 – 1000	<10
lead [1]	350 – 5000	2500 – 12000	<50
mercury [1]	<1	1 – 30	<50
tin [1]	250	1700	-
PCDD/PCDF's Total I-TEQ (see below)[2]	1-3 ng Kg^{-1}	10 ng Kg^{-1}	0.1 ng m^{-3}

1 – (Van Der Sloot et al., 1997).
2 – (Whiting, 2001).

Pollutant Distribution in Incineration Products

Many pollutants are found to some degree in bottom and fly ash, clean-up residues, and emitted gas. Their partitioning depends on the physical properties of the material concerned, and their environmental impact is affected by which product of incineration they are found in. For metals, their volatility is very important, with iron being found almost exclusively in bottom ash, whereas cadmium, which is far more volatile, is found more in fly ash [and possibly in emitted gas] (Vogg et al., 1986, Abanades et al., 2001). It has been shown that as reactor temperature increases, concentrations of volatile metals left in bottom ash decrease, implying that they must be lost to APC residue or atmosphere (Zhang et al., 2001a). It is desirable to concentrate as much as possible of the toxic material into the APC residue, which is already a hazardous substance, so that bottom ash toxicity is minimised, so long as atmospheric emissions of trace pollutants remain negligible. Nevertheless, the question remains as to what to do with the residues which arise from incineration, and the next section will consider this question. The following section will consider in detail the nature of the pollutants, and their effects, which mean that such considerations are required.

Incinerator Residue Disposal

Most bottom ash is land-filled usually after the recovery of ferrous metals by electromagnetic separators. Therefore, any pollutants remaining in the ash should not be readily leached, as this may cause contamination of waterways. Usually, bottom ash is sufficiently inert not to require additional processing. As well as disposal to landfill, processed bottom ash has also been used in the construction industry, as an aggregate, or constituent of building blocks (O'Connell, 2002).

APC residue is also land-filled, but unlike bottom ash, its composition means that it must be disposed of as hazardous waste (due to the heavy metal and trace organic contaminants), and pre-processing is required, in order to reduce the leaching of pollutants from the residue. Weathering, chemical treatment, or thermal treatment (vitrification) are most common. An unfortunate side-effect of the vitrification process is possible release of volatile metal species during the process. Also, processing may lead to worsened leaching characteristics for some metals (e.g. chromium), despite reducing overall leaching, due to the different chemical reactions which occur in the process (Kirk et al., 2002, Yoshiie et al., 2002, Evans and Williams, 2000, Park and Heo, 2002a, Park and Heo, 2002b).It is an unfortunate reality that as APC technology improves, the amount and toxicity of the residue tends to increase. It is possible that metal extraction for re-use may become viable, but this option does not seem to have received a great deal of attention as yet (O'Connell, 2002). However, as the pressure to increase environmental standards rises, and final disposal costs increase, it is to be anticipated that the pressure to recover metals from wastes will increase. Several

groups have investigated such technologies, with one claiming the ability to extract heavy metals from solution at the parts per million (ppm) levels in an environmentally and economically viable way, using reactive polymers (Tiravanti et al., 1996). Wet gas cleaning processes may lead to liquid residues, but the toxicity of liquid from wet scrubbers, and associated disposal problems has resulted in them being used very little in the UK, with dry or semi-dry clean-up being preferred (O'Connell, 2002, Williams, 2005). .

Finally, the incineration process produces stack gas. This is composed primarily of carbon dioxide and water, with small amounts of hydrogen chloride and fluoride, sulphur dioxide, oxides of nitrogen, dust, carbon monoxide, organic products of incomplete combustion, and trace amounts of heavy metals, dioxins and furans. Although the concentration of pollutants in the stack gas is low, the volumes produced are large, and once the gases have passed through the APC system, the plant operator has no control over where these pollutants end up once they leave the stack. The only control possible is to ensure that the stack is tall enough to ensure that the gases will dilute with the air, and become distributed over a wide area, so that ground-level concentrations arising from the process are not harmful (Williams and Evans, 2001, European Community Legislation, 2000a). This is why, despite very low concentrations of pollutants, the effect of this incineration product must always be considered carefully, along with the effect of the solid products.

The next section will examine the nature of the pollutants encountered during incineration, why they are of environmental and toxicological concern, and how their effect can be minimised during waste incineration.

Organic Pollutants

Organic pollutants arising from incineration have two likely sources; either they were present in the incinerator feed and were not destroyed, or they were formed from products of incomplete combustion (PICs) during the incineration process. Organic pollutants are typically highly stable species, with long half-lives in the environment. Examples include polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs). These families of organic compounds encompass a large number of specific molecules, each of which has different toxicities. Rather than quantify each one individually, toxic equivalence schemes (TE, TEQ) have been established, to allow easy comparison of total harmful organic compound output as shown in Figure 5 (Hester and Harrison, 1994, Van den Berg et al., 1998).

Equivalence factors for dibenzo-p-dioxins and dibenzofurans For the determination of the total concentration (TE) of dioxins and furans, the mass concentrations of the following dibenzo-p-dioxins and dibenzofurans shall be multiplied by the following equivalence factors before summing:	
2,3,7,8 — Tetrachlorodibenzodioxin (TCDD)	1
1,2,3,7,8 — Pentachlorodibenzodioxin (PeCDD)	0.5
1,2,3,4,7,8 — Hexachlorodibenzodioxin (HxCDD)	0.1
1,2,3,6,7,8 — Hexachlorodibenzodioxin (HxCDD)	0.1
1,2,3,7,8,9 — Hexachlorodibenzodioxin (HxCDD)	0.1
1,2,3,4,6,7,8 — Heptachlorodibenzodioxin (HpCDD)	0.01
— Octachlorodibenzodioxin (OCDD)	0.001
2,3,7,8 — Tetrachlorodibenzofuran (TCDF)	0.1
2,3,4,7,8 — Pentachlorodibenzofuran (PeCDF)	0.5
1,2,3,7,8 — Pentachlorodibenzofuran (PeCDF)	0.05
1,2,3,4,7,8 — Hexachlorodibenzofuran (HxCDF)	0.1
1,2,3,6,7,8 — Hexachlorodibenzofuran (HxCDF)	0.1
1,2,3,7,8,9 — Hexachlorodibenzofuran (HxCDF)	0.1
2,3,4,6,7,8 — Hexachlorodibenzofuran (HxCDF)	0.1
1,2,3,4,6,7,8 — Heptachlorodibenzofuran (HpCDF)	0.01
1,2,3,4,7,8,9 — Heptachlorodibenzofuran (HpCDF)	0.01
— Octachlorodibenzofuran (OCDF)	0.001

Figure 5: Toxic equivalences for different dioxins and furans (European Community Legislation, 2000a)

In waste incineration, the concentration of such molecules in the waste feed is normally small. Consequently, concentrations in bottom ash are low, as organic pollutants tend to form in the energy recovery part of the incinerator, which is at optimal temperature for the reactions required (Van Der Sloot et al., 1997, Hester and Harrison, 1994), Unfortunately, the plant temperature regime required for efficient heat energy recovery, (i.e. a reduced rate of gas cooling) allow gases to remain in the "temperature formation window" for a longer time, and thus APC residue and stack gas are at risk from organic pollutants.

While it may be possible to remove organic pollutants from the gas stream, a more preferable approach is to prevent their re-formation, through careful control of incinerator conditions. Burner and flue temperature, gas composition, redox environment and the presence of species, which may catalyse reactions (i.e. particulates) are all factors known to influence organic pollutant production, and incinerator design and operation specifications are designed to ensure (as far as possible) complete burn-out of organic pollutants (Williams, 1998, European Community Legislation, 2000a). Nevertheless, some production of organic pollutants is unavoidable, and the gas clean-up, which usually includes activated carbon injection to absorb organic pollutants, ensures that the stack gas concentrations are acceptable Table 5). Performance is monitored with a combination of continuous process monitoring for CO (the simplest product of incomplete combustion) and general "organic content", and twice yearly more comprehensive testing for the most toxic organic pollutants from combustion, dioxins and furans (Williams, 2005, European Community Legislation, 2000a).

Inorganic Pollutants

The main inorganic pollutants of concern are metals and metalloids, notably heavy metals such as cadmium, lead, and mercury. Whilst the form (i.e. oxidation state and

compound) of the pollutant may well be significant, limits are set for total elemental output, with the EU and US having slightly differing specified metal lists, and maximum permissible concentrations (Hester and Harrison, 1994, European Community Legislation, 2000c).

Volatile metal species tend to be found largely as small (<10μm) particulates (PM_{10}) in the stack gas, though these are largely removed by the air pollution control devices (Table 5). Less volatile metals are found in the bottom ash. Unlike organic pollutants, metals which are present in the incinerator feed must ultimately be present in the incinerator output, either in gaseous emissions or solid residue, as elementally they cannot be destroyed (though their speciation may change). Therefore, the aim in control of these components must be subtly different from those for organic pollutants. If the metals cannot be removed from the feed (often the most desirable solution), their effect in the incinerator output must be minimised. Presence as particulates in flue gas is seen as highly undesirable, as their distribution cannot then be controlled, and such small particles can become trapped in the lungs, where the physiological effects of toxic metal compounds tends to be particularly significant.

Therefore, it is the more volatile metals, such as lead, cadmium and mercury, which cause the most concern. Nevertheless, the concentration of these metals in the APC residue is not a particular problem, provided that atmospheric emissions are minimised (Williams, 2005). Although it would also be desirable from an environmental point of view to convert metal containing species into the least toxic compound possible, legislative limits do not encourage this practice as they merely set maximum concentrations for a given metal, in a given residue, although non-leachable forms are favoured. (Williams, 2005). However, ever since the first experimental investigations of metal partitioning in an incinerator, there has been a great deal of interest in how metals behave under these conditions (Brunner and Monch, 1986, Linak and Wendt, 1993).

Information on the partitioning of different metals between different residues, and the reactive processes causing transportation of these metals is limited (Lockwood and Yousif, 2000, Morf et al., 2000, Linak and Wendt, 1993). Analysis is made more complex by the variability and lack of homogeneity of the residues, which can make sampling errors highly significant (Reimann, 1989). The data on gaseous emissions is even more limited, with traditional analysis techniques only allowing average values to be obtained, and with legislative drivers only requiring the measurement of specific metals, and at relatively infrequent intervals. New data on the presence of volatile toxic metals in incineration, their behaviour, and their variation with time would be highly useful for an improved understanding of the processes involved, which should lead to improved incinerator operation. A more detailed review of the information available on metallic pollutants will be made in section 2.2.

2.1.7 Technological Improvements to the Waste Incineration Process

Having established that emissions from incinerators are a justifiable cause for concern, the technological implementation of the incineration process can help to minimise the environmental effects. By employing efficient combustion, clean-up and monitoring technology, the negative impact of incineration can be minimised.

Combustion Chamber Technology

The exact design of the combustion chamber is important in determining how efficient and effective the combustion process is. To minimise pollution from incineration, it is essential that the waste is fully combusted, at high temperature. Therefore, EU legislation states that the gases from incineration must always be exposed to a temperature of 850 °C for 2 seconds (European Community Legislation, 2000a).

The exact design of the combustion chamber (grate type, geometry, air injection) will have an effect on the combustion efficiency, and associated pollution, but is not specified in the legislation. Thus a large number of combustion chamber designs exist, all of which function slightly differently (e.g. rocker grate, stocker grate, forward reciprocating grate, reverse reciprocating grate) (Williams, 2005). Modern computational methods, when applied to existing incineration plants, have suggested that relatively minor changes to the combustion chamber (e.g. its internal geometry) could have a substantial effect in improving combustion efficiency, as may changing the way in which waste is fed into the combustion chamber (Nasserzadeh et al., 1995, Hart, 2001). Such new information means that newly designed incinerators may be much better designed than previously.

Despite the wide variety of different deigns employed for the combustion chamber, most possess a variety of common features: a means of introducing waste to the combustion process, a means of transporting waste and incineration residues through the furnace (moving grate), refractory and high-temperature steel enclosure (usually with means of energy recovery by steam generation), injection of primary air below the grate, and injection of secondary air (to ensure complete combustion of organic components) above the grate. How these elements are incorporated in the design, and how they are operated during plant use, will have an effect on the combustion process, and the pollutants which arise from the process (Williams, 2005, Daniel et al., 1988), and although each design cannot be considered in detail here, the effect of these on combustion efficiency cannot be ignored.

Air Pollution Control Technology

Historically, flue gases from incinerators contained many different polluting materials at high concentrations, which were released to the atmosphere. However, as environmental awareness and regulatory burden grew, pre-release clean-up of gas streams became an integral part of the incineration process. Initially, water sprays, cyclones and electrostatic precipitators were used to remove particulate matter (Greenberg et al., 1978). As technology has progressed, these have been replaced in the UK with sophisticated scrubbers and bag filters, which remove many pollutants, notably particulates, acidic and corrosive gases, heavy metals, and organic products of incomplete combustion (Hester and Harrison, 1994). However, throughout the world, a variety of different devices, with different specifications, are still used (Russel and Vogel, 2003, Kefa et al., 2003).

Cyclones use centrifugal force to cause particulates caught in the gas stream to collect on the walls of a conical container. Dirty flue gas is pumped axially into the container, and follows a helical path down the cyclone. Particles collect on the cyclone walls, and drop down to a dust collector beneath. When the gas reaches the bottom of the cyclone, it forms a vortex, and flows back up the centre of the cyclone, and out of the top of the device. This allows the removal of larger particulates, down to about 15 μm. This allows some clean-up of the gas, but alone does not provide sufficient particulate

removal to meet current EU regulations (Williams, 2005, European Community Legislation, 2000a).

In an electrostatic precipitator (ESP), an electrostatic field is used to give particulates a negative charge. The particulates in the flue gases then collect on the positive electrode, which is periodically cleaned by physical means, the extracted dust being collected and disposed of. Between 97% – 99.5% of particulates can be removed by an efficient EP, and the contaminants need not be solid (i.e. may be liquid or tar) for effective removal. Removal of particles down to less than 1 μm is possible. This technology is used in many countries, but is not capable of reliably meeting current EU regulations, as ESP's are relatively inefficient at removing small particulates between 0.1 μm and 1.0 μm (Linak and Wendt, 1993, European Community Legislation, 2000a).

Large fabric filters (baghouse filters) are an essential part of gas clean-up, in order to meet current emissions limits (European Community Legislation, 2000a, Hester and Harrison, 1994). Very small particulates are trapped on fabric filters, which are periodically cleaned by pulsing air through them, counter to the normal flow of flue gas. Collected dust falls due to gravity, and is collected in a sealed container. As particulates build up, this tends to increase trapping efficacy, but will reduce flow through the filter.

In a wet scrubber, flue gases are passed counter-current to a spray or fine mist of absorbent liquid, such as a solution of lime or calcium hydroxide, and pollutants are removed by chemical reaction. Acidic flue gases, such as SO_2, HCL, HF dissolve, and are removed from the flue gas. The resulting acidic liquid then removes soluble metal species. Removal efficiencies are high (>90%), but the system has drawbacks; the flue gases are cooled, and become moisture-saturated, which means they have to be re-heated before exhausting to air, which is energy-inefficient, and large volumes of polluted liquid are produced, which require processing before they can be disposed of (Williams, 2005).

A further development of the Scrubber arrangement is the dry or semi-dry scrubber. Instead of a liquid, dry fine particles, or saturated droplets are injected counter to the flue flow. Lime is used to adsorb acidic gases. In the semi-dry scrubber, the flue gas temperature is sufficient to desiccate the lime droplets, giving particulates which can be collected. Activated carbon can be used to remove heavy metal and dioxins/furans. Resultant contaminated particles are collected in downstream fabric filters, and can be re-cycled several times before being unable to adsorb further material. Dry scrubbers can operate at a higher temperature than wet scrubbers, so are more energy efficient. Removal efficiencies may be slightly lower than for a wet scrubber, but the technique tends to be preferred due to the reduced production of contaminated waste streams. (Williams, 2005).

Selective catalytic reduction (SCR) of nitrogen oxides is possible with a transition metal catalyst, and the addition of ammonia or urea. Water and N_2 are produced. Heavy metals deactivate the catalyst, so the process takes place after the fabric filters. NO_x is found in flue gases from combustion of N-containing fuels, and also from high temperature combination of molecular N_2 and O_2 during the combustion process. Careful process (gas composition, temperature) control can limit NO_x formation, so

many plants operate without this control technology, though it is to be expected that its use may become mandatory in the future (Williams, 2005).

Assessing Pollution from Industrial Processes

Having established that the products from a process such as incineration may be toxic, monitoring of emissions must take place, as well as safe limits being set. Emissions monitoring is thus conducted for three main reasons; to ensure that legislative requirements are being met, to optimise process to minimise emissions, and to demonstrate to the public that a process is being run in an environmentally responsible manner possible (Scott, 1995, Meyer, 1995).

It is not currently possible to continuously monitor the vast number of possible organic and inorganic emissions from incinerator stacks, and periodically, discrete samples are analysed for dioxin and metal content. CO, NO_X, SO_2, HF, and HCl are monitored continuously, along with incinerator temperature, to ensure legislative compliance. CO is released during incomplete combustion, and thus acts as a surrogate indicator for conditions likely to cause high levels of dioxin emission. High temperature combustion would make high metal emissions likely.

Although continuous monitoring of metals and metalloids is not yet required, it is to be expected that such monitoring will one day become mandatory, with current EC legislation indicating that the introduction of such measurement techniques is expected, when the technology becomes available (European Community Legislation, 2000a). There is therefore currently significant research interest in new continuous emissions monitoring technologies for metals.

So it is seen that incineration is set to play a significant role in municipal waste management for the foreseeable future, and that despite careful controls on operation, in order to minimise potentially harmful emissions, further work is still required to optimise incineration processes, and improve public acceptability of this waste management option. Subsequent work reported in this thesis concentrates on the occurrence, measurement, and effects of metallic pollution from incineration, and considers how improved process engineering can help to understand the processes leading to metal emissions, with a view to their minimisation.

2.2 Metals in Municipal Solid Waste Incineration

2.2.1 The Fate of Metals in Incinerators

The problem of metals in incinerated waste was introduced in section 2.1.6. As explained, metals are elements, which cannot be created nor destroyed, and so any metals present in incinerated waste must be found in the incinerator output (bottom ash, APC residue, or stack gas). The chemical speciation of the metal may change, as the metal component may react chemically to form a new compound, but the amount of total metal will be constant. The partitioning of metals between the residues is a complex process which is incompletely understood (Reimann, 1989, Linak and Wendt, 1993).

Key variables identified in determining metal partitioning are:

- The nature of the incoming waste – the physical and chemical nature of the incoming metal of interest, and of the waste matrix.

- The physical-chemical properties of that metal – its boiling point, reactivity etc.
- The physical-chemical environment in the furnace – temperature, reactive gases and particles present, residence time.
- The physical-chemical properties of the flue gas treatment system – temperature, rate of cooling, pollution control devices, reactive and non-reactive sorbents.

Inert (non-combustible, non-volatile) solids remain on the grate, and exit the incinerator in the bottom or grate ash. For most metals, we may think of this as the "default", unless some active process occurs to cause its removal from the burning bed. If the metal (in any chemical form) is to leave the burning bed other than in the bottom ash, it must be via the raw flue gases. An active transport process must occur to transport the metal with the flue gases, and two possible mechanisms exist. For volatile metals, the heating of the metal in the furnace may cause it to evaporate, and the vapour will be transported through the incinerator along with other gaseous combustion products. Alternatively, for non-volatile metals, small solid particulates containing the metal may be entrained in the gas stream (Linak and Wendt, 1993, Belevi and Moench, 2000a). Thus volatilisation and entrainment are the two most important processes in metal transport in incinerators, and anything which affects these processes is therefore of interest.

Air pollution control (APC) devices are designed to minimise the atmospheric pollution by capturing pollutants as solid or liquid residues. For metals, this means capturing the entrained metal particles, and the particles or liquid droplets which have arisen from metal volatilisation, but which may since have coagulated and/or condensed. Capture of metals does not eliminate the problem of metals from incineration, as the APC residue will contain these components, but these are much more manageable than the uncontrolled release of pollutants to the atmosphere (Hester and Harrison, 1994).

If a material which entered the incinerator did not remain in the bottom ash, and was not removed by the APC system, it must be present in the emitted stack gas, as there is no other route which it could have taken out of the incinerator. It has been noted earlier that the emission of metals in the stack gas is undesirable, , and therefore it is imperative to ensure that incinerator APC's are designed to remove as near as possible all metals which were released from the burning bed.

In the following section, the different factors which determine metal partitioning will be examined, and it will be shown how manipulation of these different variables can effect changes in metal partitioning, with the aim of minimising the impact of metal pollutants in waste incinerators.

2.2.2 Factors Affecting Metal Partitioning

It has been explained that any metal entering the incinerator must exit the incinerator in the bottom ash, APC residue, or stack gas. The proportion of different metals found in each residue changes from sample to sample, and from incinerator to incinerator. This may due in part to differences in metal content of the incoming waste stream, but it is apparent that the partitioning characteristics of different metals are different, and that for a given metal, the partitioning changes with other changes in the incinerator operating environment. The subsequent sections show what is known about how the partitioning of a metal may be altered, and how this could be exploited to achieve a desired outcome.

The Nature of the Incoming Waste

It should be evident that the physical and chemical nature of the incoming waste may affect the partitioning of the metal within the incinerator. For instance, lead is found in metallic form, in batteries and leaded solder, which is found on printed circuit boards in all electronic items [prior to it's prohibition in 2006] (European Community Legislation, 2002b). Lead is also present in waste in lead compounds in paints, dyes and plastics, although the trend is towards the decreased general use of lead compounds (Linak and Wendt, 1993, Thompson, 2004). Clearly, a reduction in the amount of lead entering the incinerator will result in a reduction to the amount in the incineration residues. Previously, differentiation has been made between metals which were intimately associated with combustible fuel, and those which were present in non-combustible components of waste (Law and Gordon, 1979), and it was concluded that silver, cadmium, chromium, manganese, lead, tin and zinc emissions could be reduced by the selective removal of non-combustible material from the waste stream. They also suggested that the emissions of aluminium, barium, cobalt, iron, lithium, sodium, nickel and antimony might be reduced by the same means.

Furthermore, each lead compound will have different thermodynamic and chemical properties, such as boiling point and reactivity, and as such will behave differently in the furnace. The physical nature of the metallic input to the incinerator may also be important. Residence times are sufficiently short that non-equilibrium kinetic conditions may apply in the incinerator environment, and particle size may dictate how completely reactions can occur within the limited time available in the incinerator, and thus large metallic items may behave very differently from disperse metal particles. For example, a leaded solder joint on a printed circuit board is likely to behave significantly differently from a lead stabiliser in a PVC plastic product, which again will behave differently from the lead in a large lead-acid battery (Linak and Wendt, 1993, Lockwood and Yousif, 2000). Metals which are present as components of combustible waste will therefore behave very differently from those present in "non-combustible" bulk waste items, which may be largely unaffected by the combustion process (Law and Gordon, 1979).

The nature of the surrounding waste matrix is also known to affect the partitioning of metals between the different incinerator residues. In addition to the characteristics of the incoming metal of interest, the characteristics of the remaining incoming waste at the same time will affect metal distribution (Williams and Evans, 2001, Linak and Wendt, 1993). It has even been observed that the method of introduction of the waste to the incinerator may affect partitioning (Linak and Wendt, 1993). This applies particularly to hazardous liquid wastes, which may be fed continuously, or batch-wise, (e.g. in barrels). The logical inference from this finding is that good mixing of municipal waste will tend to remove localised regions of high concentrations of a particular species, and so minimise the effect of local conditions on partitioning behaviour.

Volatile metals may be removed from the burning bed, into the flue gases, by evaporation. Often, however, the metal chloride is more volatile than the metal itself, and formation of the metal chloride, or even other metal compounds, is significant to metal transport (Abbas et al., 1996, Perry and Green, 1998, Linak and Wendt, 1993). Where the concentration of different metals is high and of chlorine and other anions low, the transport mechanism may become saturated. As a result the partitioning of a

particular metal can change with the amount of that metal, other metals, and different anions in the feed. F, Cu, Mo, Pb, Sn, Zn, Br and Sb have been identified as being sensitive to variations in input quantity and physical form (Belevi and Moench, 2000b). However, the factors described above are all physical characteristics of the waste input. These are difficult to manipulate for a mass-burn incinerator. Some plants do sort incoming waste, or process it (e.g. by shredding), but it is generally found that such additional processing is uneconomic (Williams, 1998), although it may be highly environmentally beneficial (Rydh and Karlstrom, 2002).

The chloride anion, particularly as provided by the burning of PVC, has been identified as a species critical in increasing the carry-over of semi-volatile metals from the furnace to the gas phase. The chloride anion (or radical) is able to convert metals to metal chlorides (and potentially other metal species to metal chlorides). In general, the chloride of a metal is more volatile than the metal itself, so allows for increased transfer from the solid to the gas phase, and so evaporative transport from the burning bed (Linak and Wendt, 1993, Evans and Williams, 2000, Zhang et al., 2001a). The nature of the incoming chloride has also been shown to be important (Wey et al., 1999); they demonstrate that while chlorine present in PVC affects metal partitioning, inorganic chloride from sodium does not affect metal partitioning. It is thus evident that a complex mixture of physical factors, chemical thermodynamics and kinetics determine the partitioning of metals. Having identified the importance of the chloride anion, some groups have suggested the tailoring of incinerator parameters to enhance metal carry-over, in order that APC residue will be further enhanced in trace metals. However, to date, there appears to be no practical utilisation of such theories, possibly because of problems of corrosion and deposition caused by these metal salts (Belevi and Moench, 2000b, Bryers, 1996).

The effect of other anions such as sulphur and oxygen may also be important (Linak and Wendt, 1993). Although metal sulphates are normally more volatile than the native metal, sulphates may reduce transfer of metal to the gas phase by competing with the even more volatile metal chlorides. Even the moisture content of the waste may affect metal partitioning and reaction chemistry in the burning bed (Zhao et al., 2004).

Having considered aspects of the chemistry of the waste matrix which may enhance transfer of metals from the burning bed, it is prudent also to consider factors which may enhance their retention in the bottom ash. Although data is sparse for waste combustion, much has been obtained on coal combustion, and this suggests that silicates (Si_2O_3) and aluminosilicates (SiO_2Al2O_3) may help to trap trace metals in the bottom ash (Linak and Wendt, 1993). Silicates and aluminosilicates are usually present in the fuel as their sodium salt, but the sodium cation may be displaced, for example by potassium, or by a heavy metal ion.

Numerous experiments have been conducted to investigate the effect of such absorbent materials on heavy metal partitioning. Some have investigated reactive sorbents in the gas clean-up system, at relatively low temperatures (Uberoi and Shadman, 1990, Uberoi and Shadman, 1991a), while others have considered absorbtion in conditions approximating to those found in the furnace (Chen et al., 1997, Chen et al., 2001). For sorbents at furnace temperatures it has been shown that both chemical reaction and physical absorption play a role in trapping the metal in the furnace bed, although, it is dubious whether simulated conditions accurately reflect real incinerator conditions.

Nevertheless, such experiments help to indicate how the matrix surrounding a metal on the burning bed of an incinerator may help to trap it in the bottom ash.

Thus it is seen how changes in metal concentration in the incoming waste to an incinerator may affect pollutant concentrations in the different residues, and the percentage partitioning between those residues. It is therefore significant that the concentration of different metals in the waste differs, as would be expected, and the range for a given metal is also highly variable, corresponding to a highly diverse waste stream. This can be seen in Table 6, which shows the elemental composition of municipal waste as analysed in a number of different studies. It is important to remember that variations in data given by different groups may reflect different source waste compositions in different areas or at different times, as well as different sampling and analysis techniques.

Table 6: The composition of municipal solid waste as reported by different groups

metal	USA[1] (g tonne^{-1})	Europe[2] (g tonne^{-1})	Vogg[3] (g tonne^{-1})	Belevi & Moench[4] (g tonne^{-1})	Wiles, 1996[5] (g tonne^{-1})	International ash working group (1997)[6] (g tonne^{-1})
aluminium				11000 - 13000	22000-73000	
antimony			50	41 - 74		10-60
arsenic				2.7 - 4.1		3-9
barium				370 - 430	400-3000	730
bromine				110 - 140		
cadmium	2 – 22	10 - 40	20	11	0.3-71	5-15
calcium				24000	37000-120000	10000-35000
chlorine		5000 - 15000		6900 - 7300	800-4200	
chromium	20 – 100	100 - 450	-	310 - 360	23-3200	40-400
cobalt				3.4 - 3.7		
copper	80-900	450-2500	100	780 - 820	190-8200	200-1000
fluorine		50 - 250		180 - 210		
iron	1000 - 3500	25000 - 75000	-	27000 - 31000	4100-150000	25000-50000
lead	110 – 1500	750 - 2500	1500	530 - 700	98-14000	400-1000
lithium				9 - 10		
magnesium				3200	400-26000	
manganese				220 - 270	83-2400	200-500
mercury	0.7 – 1.9	2 - 7	5	2.9 - 4.2	0.02-7.8	0.5-5
molybdenum				9 - 11		
nickel	9 – 90	50 - 200	-	100 - 110	7--4300	20-130
phosphorus				690 - 960		
potassium				2300 – 2500	750-16000	5000
silicon				37000 - 38000		
sodium				4800 - 5100	2900-42000	3000-15000
sulphur		2000 - 7000		1300 - 1400	1000-5000	
tin				71 - 74		120
titanium				1500		1300
zinc	200 – 2500	900 - 3500	3000	1300 - 1600	610-7800	600-2000

[1] (Law and Gordon, 1979)
[2] (Williams, 1998)
[3] (Vogg et al., 1986)
[4] (Belevi and Moench, 2000b)
[5] International Ash working group, 1994, reported in (Wiles, 1996)
[6] (Van Der Sloot et al., 1997)

The Physical-Chemical Properties of the Metal of Interest

For a given metal, physical and chemical properties will affect metal partitioning. For example, cadmium metal boils at 1035 K, so at the temperature of a MSW incinerator, the metal may evaporate, and be carried as a gas out of the burning bed. In contrast, nickel only sublimes at 3000 K, well above the temperature in an incinerator, and so an evaporative transfer route is not significant for that metal, although nickel compounds may be volatile. Any of these species may exhibit significant volatility below their boiling point, if they have a high vapour pressure, so in considering a complete model of metal behaviour, it is insufficient to consider boiling point alone, (although it is a good initial indicator) and a more sophisticated model of metal volatility is required. Table 7 indicates the boiling points of various metal-containing species, and shows why chlorine helps mobilise metals, because chlorides are often more volatile than the metals themselves. It is therefore important to consider both the speciation of the metal entering the incinerator, and furnace conditions which may allow reaction of the metal to form new compounds in-situ (Linak and Wendt, 1993, Paoletti et al., 2001).

Table 7: Difference in boiling point between metals and their compounds (Abbas et al., 1996)

compound	Cd	CdO	$CdCl_2$	Zn	ZnO	$ZnCl_2$	Ni	NiO	$NiCl_2$
boiling point (K)	1035	1832*	1240	1180	1700*	1005	3000	3000	1260

*** Denotes sublimation.**

The Physical-Chemical Environment in the Furnace

Having seen that the volatility of a metal will affect its partitioning, the converse of this is that for a given species, changing the furnace temperature will affect its partitioning (Belevi and Moench, 2000b). Changing the temperature will also affect chemical reactions occurring, and thus is likely to affect the metal partitioning (Delay et al., 2001). For example the rather exotic species CrO_2Cl_2 is predicted, by some thermodynamic models, to exist only in a narrow temperature window around 425°C (Linak and Wendt, 1993).

If chemical reaction is to be important in determining metal partitioning, then reaction environment will be vital. In waste incineration, the average temperature in the furnace generally is around 800-950°C, with additional burners operating if the temperature falls below 750°C, and waste supply being cut if temperature rises over 950°C (although flame temperatures in specific regions may be much higher) . The excess air under which the incinerator is operated will affect the redox conditions in the burning bed, and so will affect redox reactions of metal species. Thus it is reactions which can occur in this sort of environment which must be considered when studying the effects of reactivity on metal partitioning (Williams, 2005, Yang et al., 2002, Paoletti et al., 2001).

It is also thought that excessive under-fire air may enhance entrainment of dust particles, and that water content and calorific value of the waste may affect metal partitioning (Brunner and Monch, 1986, Morf et al., 2000). As entrainment is known to affect metal partitioning, any variable affecting this process will, in turn, affect the partitioning of metals (Williams and Evans, 2001). As at least some reactions occurring in the burning bed are known to be under kinetic control, residence time in the high-temperature combustion zone will be important (Lockwood and Yousif, 2000).

The Physical-Chemical Properties of the Flue Gas Treatment System

When the raw flue gas leaves the combustion chamber, it is a complex aerosol comprising of major, minor and trace gases, and entrained particles. Volatile metals are present as vapours, and entrained metals as particulates, of varying sizes. As the gas passes through the energy recovery and APC devices, it is subject to changes in temperature, chemical environment and speed of movement. Volatile metal vapours may cool sufficiently to re-condense, and the aerosol will mature, according to a number of processes of aerosol dynamics, which have been extensively studied (Linak and Wendt, 1993). The flue gas is subject to further chemical reaction, interaction with sorbents in scrubbers and particle capture by ESP or bag filter. Remaining gases are then released through the stack. An understanding of all the processes occurring between evolution of raw stack gas and emission of processed gas is vital to the understanding of the partitioning of metals in the flue gas.

It is important to consider chemical reactions occurring as flue gas passes through the post-combustion chamber parts of the incinerator. A specific example is antimony transport. A volatile chloride species is implicated in partitioning in the bed, but it is thought that it is converted back to Sb_2O_3 in oxygen-rich conditions in the flue system. This species would have condensed by the filters, and so would be trapped (Paoletti et al., 2001). Thus it is seen that the processes involved in the development of the flue gas, from leaving the burning bed, to the APC device, is not simple, and cannot easily be explained quantitatively.

The consensus of literature opinion is that the major constituents of fly ash (ash particles) are Cl, K, Zn, Na, Ca, Si, and Pb, Al, in the form of oxides, silicates and aluminosilicates. The trace elements usually found in fly ash are Ag, As, Br, Ce, Cr, Cu, Hg, Mg, Mn, Ni, Rb, Sb, Ti, Tl and Zr. Spherical particles are found in the ash, and are found to be aggregates of polycrystalline, amorphous and glassy material, and are mainly composed of calcium, sodium and potassium aluminosilicates of complex structure. They are also enriched in more volatile elements, which have arisen from vaporisation and condensation (Ontiveros et al., 1989, Linak and Wendt, 1993, Chang et al., 2000a, Evans and Williams, 2000).

Scanning electron microscopy-energy-dispersive-x-ray techniques have been used to show that particles are made up of agglomerations of smaller ones. Although the bulk of the larger particles is of aluminosilicate material, individual vapour depositions of specific metals can be seen on the surface (Evans and Williams, 2000). X-ray diffraction has been used to identify various metal and metal compounds deposited on flue gas particles (Wey et al., 1999), and this evidence supports the proposed routes of ash formation by entrainment and volatilisation/condensation/deposition,

The overall characteristics of the ash produced have also been investigated (Greenberg et al., 1978). A bimodal size distribution was found, with over 75% of volatile metals were found in particles of <2μm. More recently it has been shown that the size distribution of fly ash collected on a bag filter from a small-scale model incinerator is bimodal (Thipse et al., 2002). Analysis of the different fractions showed that their composition varied significantly as shown in Table 8. For instance, the 75-150 μm fraction was found to contain more than 40% of each of the total aluminium and silicon found in the fly ash. These findings for waste incineration ash support similar findings for the volatile metal content of ashes from other thermal sources, for example

from steelworks, where volatile metals are also significantly enriched on the smallest particles (McDonnell et al., 1989).

Table 8. Variation in composition of fly ash particles with size (Thipse and Dreizin, 2002)

percentage found in size fraction	total Mass	Al (%)	Cr (%)	Fe (%)	Hg (%)	Ni (%)	Pb (%)	Si (%)
0 - 75 μm	10	42	8	11	7	7	4	43
75-150 μm	28	20	12	12	19	11	16	21
150-300 μm	21	18	20	20	38	18	43	19
300-1000 μm	40	15	25	25	24	27	32	11
1000-1200 μm	1	5	35	32	12	37	5	6
overall ash composition (%)		0.12	0.025	13.35	0.069	0.028	0.03	2.11

The distribution is due to the different transport properties involved. Large particulates are transported by entrainment, whereas vapours of volatile species subsequently undergo nucleation and condensation, forming much smaller (sub-micron) particles. Coagulation and coalescence occurs as the aerosol evolves, leading to an increase in the average particle size in the aerosol (Mulholland et al., 1991, Mulholland and Sarofim, 1991, Thipse et al., 2002). A third transport mechanism has been demonstrated for viscous metal salts, involving the formation and explosive breakdown of non-volatilised particles called cenospheres (Mulholland and Sarofim, 1991). However, this mechanism only applies to a limited number of metal salts (e.g. nickel nitrate), so it is unclear how significant this pathway is.

Thus the results of a large amount of literature support the proposed transport mechanisms of entrainment and volatilisation, with subsequent nucleation, condensation and coagulation. Once these have been accepted, it can be assumed that temperature gradient, gas velocity and residence time will all affect particle size distribution (PSD). Perturbation of the PSD will affect particulate capture, and so metal partitioning (Linak and Wendt, 1993). Increased cooling rates will favour homogeneous nucleation over heterogeneous condensation, leading to more small metal particles, which will escape APC's. Gas velocity will affect coagulation and particle deposition, and residence time will alter the maturity of the developing aerosol and so the PSD will tend towards larger, more easily capturable particles with increased residence times (it is an interesting aside that greater particulate loading in the raw flue gas, i.e. from "dirtier" fuels can result in improved metal capture (Abbas et al., 1996).

The processes involved in aerosol formation and development, and their mathematical description, have been developed in detail, and are discussed in further detail in section 2.6.2. These processes are common to aerosols from a variety of thermal processes (Linak and Wendt, 1993, Barton et al., 1990). Once a vapour has been formed, and the temperature of the gas then drops, homogeneous nucleation or heterogeneous condensation onto existing particles occurs, giving minute (nanometre) particles of metal or metal salt. Condensation may occur onto any existing particle of any size, but the relative surface area of small particles is much larger than that of large particles, and thus there is more metal deposition on the smaller ones, leading to the observed enrichment of volatile metals on sub-micrometer particles (Greenberg et al., 1978).

The minute particles formed by nucleation would have no hope of being trapped by APC devices, but fortunately the exhaust aerosol develops further before reaching them. These particles tend to collide with one another, which may lead to coagulation,

with adhesion or agglomeration causing larger particles. Provided that the aerosol is sufficiently developed before it reaches the APC device, particles should have grown large enough for capture (Linak and Wendt, 1993). This supports the observation that many of the larger particles are agglomerations of smaller ones (Evans and Williams, 2000). Once more surface area to volume considerations ensure that coagulation tends to occur more between small particles, maintaining enrichment of metals in the sub-micron ash fraction. Thus it is been explained how the observed size distribution and composition of ash particles arises from the different transport mechanisms, of entrainment, and vaporisation (with subsequent nucleation, condensation and coagulation)

However, the presence of reactive capture systems must also be considered for a complete understanding of the behaviour of metals in waste incineration. Scrubbing systems were introduced with the intention of reducing emissions of acidic gases, such as HCl and SO_x. They operate by the injection of a sorbent, typically slaked lime [$Ca(OH)_2$] which reacts with the acidic gas, forming solid calcium salts, which are subsequently removed by the particulate capture system. It was found that these systems also reduced metal emissions significantly. There are two possible reasons for this, one being the reaction of metallic species with the sorbent, and the other being the physical trapping of metallic species by scrubber particles or droplets, and their subsequent capture (Linak and Wendt, 1993, Lockwood and Yousif, 2000). In either case, the larger solid particulates formed are captured more effectively by the capture device. Some systems now simultaneously inject activated carbon, which is an effective reactive absorbent for small residual amounts of metallic vapours (mainly mercury and possibly cadmium), and also residual organic pollutants (Morf et al., 2000).

Injected sorbents can behave like any other particulates in the flue gas aerosol, acting as nucleation points for volatile metal vapours below their saturation point, and as surfaces for coagulation. However, statistical analysis of the metal concentrations observed on different particles, and experiments on desorption of metals from sorbents indicated that reactive absorption mechanisms, known as chemisorption, also occur, (Linak and Wendt, 1993, Evans and Williams, 2000, Lockwood and Yousif, 2000, Chen et al., 2001, Uberoi and Shadman, 1991b). The effect of reactive absorbent processes is that more than one factor, including chemical identity of the absorbent, and the available surface area for absorption, which is not (necessarily) the same as total measured surface area, affect metal capture. Thus the process can no longer be accurately mathematically described, as its complexity increases significantly (Williams and Evans, 2001, Evans and Williams, 2000).

Finally, the particulate removal part of the APC system must be considered when examining metal partitioning. In order to minimise atmospheric emissions, development of particle removal technology has been significant in the last 30 years or so, as explained in section 2.1.7. As shown in Table 9, the different technologies available do reduce atmospheric emissions significantly, and so play a significant role in determining the partitioning of material between APC residue and flue gas. Particle capture efficiency by bag filters is size dependent, and for ESP's is dependent on size and electronic properties, so the choice of system affects how well metals are captured.

Table 9: Levels of pollutant found before and after APC device (mg m^{-3}) (Williams, 1990)

pollutant	raw gas	cyclone	ESP	ESP + wet scrubber	ESP + dry scrubber
dust	3000	500	100	50	50
HCl	1150	1150	1150	50	50
HF	9	9	9	1	1
SO_x	500	500	500	100	250
NO_x	250	250	250	150	150
Pb	30	9	3	1.0	0.2
Cd	1.8	0.3	0.2	0.04	0.02
Hg	0.5	0.5	0.5	0.3	0.05

Electrostatic precipitators and bag filters remove particulate matter from the flue gas in a non-selective matter. They are least effective for very small particulates, and for vapours, although bag filters are significantly more efficient than ESP's at particulate capture, with typical removal efficiencies in excess of 99.9 %. Consequently, mercury is poorly trapped, unless activated carbon injection is employed, as it often passes through the APC device as a vapour (Chang et al., 2000b).

Investigations at a Taiwanese incinerator revealed an overall particulates removal efficiency of 99.93% for the dry lime scrubber and bag filter. Examination of the particle size distribution showed that 70% of the material was less than 4.6 μm, in diameter. Metal depositions on the different fractions were such that around 80% of the Cu, Pb and Zn was found to be found on the 70% of the particles of less than 4.6 μm (Table 10) (Chang et al., 2000b). Thus it is seen that effective small particulate capture is required for effective metal removal from the raw flue gas of waste incinerators.

Table 10: The mass and composition of particles collected before the APC device (Chang et al., 2000b)

metal	concentration (mg Nm^{-3})*	particles <4.6 μm	particles 4.6-10 .9μm
Zn	15.5 – 260	75 - 92	8 – 25
Pb	6.3 - 26.0	80 - 96	4 – 20
Cu	1.1 - 1.6	75 - 94	6 – 25

***N Denotes normal cubic meter, with 11% O_2 dry gas at atmospheric pressure and 273 K**

The result of an effective APC system is a much cleaner flue gas emission to the atmosphere, and a solid APC residue requiring further treatment and disposal, at the rate of about 60kg of residue per tonne of waste incinerated (Wiles, 1996). Typical analyses of this residue are given in Table 11. It can be seen that in general, newer incinerators have better capture of metals than older ones, although a changing input waste composition may complicate comparison of the data. It should be noted that the vastly different values for calcium correspond to whether or not a calcium compound is used in gas clean-up, and in order to compare data, it may be necessary to normalise with respect to calcium. It is interesting to note that the wet scrubber gives much better removals than dry techniques do, but despite this dry techniques are generally favoured at present, because liquid residues from wet scrubbing present a significant disposal problem (Williams, 1998).

Table 11: Typical APC residue metals analyses (g tonne^{-1})

group reference	sample	Al	Ba	Ca	Cd	Cr	Cu	Fe	Hg	K
Brunner & Moench, 1986	ESP dust				260		1100	30000	8	-
Ontinveros, et al., 1989	$CaCO_3$ scrubber + bags	79600	1940	60000	230	420	780	13400	-	10134
	wet NaOH scrubber + bags	-	2353	9800	597	35	1900	-	-	39200
Evans and Williams, 2000	post-1990 Incinerator	-	-	-	67	-	318	1560	<2	-
	certified reference material (old?)	-	-	-	361	-	1052	18460	16	-
	certified values	-	-	-	470	-	1302	21300	31	-
Belevi & Moench, 2000b	APC residue	33000	1800	175000	410	740	1090	9600	90	29000
Wiles, 1996[1]	dry/semidry APC residue	12000-83000	51-14000	110000-350000	140-300	73-570	16-1700	2600-71000	0.1-51	5900-4000

(Table 11continued)

group reference	sample	Mg	Mn	Na	Ni	Pb	Zn	F	S	Cl
Brunner & Monch, 1986	ESP dust	-	-	-	-	6200	32000	2000	28000	54000
Ontinveros, et al., 1989	$CaCO_3$ scrubber + bags	15900	910	16100	200	8380	-	-	-	-
	wet NaOH scrubber + bags	-	-	37350	50	4271	-	-	-	-
Evans and Williams, 2000	post-1990 Incinerator	-	-	-	-	780	5418	-	-	-
	certified reference material (old?)	-	-	-	100	7900	21057	-	-	-
	certified values	-	-	-	123	10870	25770	-	-	-
Belevi & Moench, 2000b	APC residue	38000	550	38000	120	14400	36000	5100	3000	282000
Wiles, 1996[1]	dry/semidry APC residue	5100-14000	200-900	7600-29000	19-710	2500-10000	7000-20000	-	1400-25000	62000-380000

[1]. **Data from the IAWG, 1994, as reported in (Wiles, 1996)**

Following effective APC systems, the final emissions of metals to the atmosphere are extremely low, as shown in Table 12. Thus it is clear that the APC system, and the associated processes occurring during aerosol development, have an enormous effect on the partitioning of metals from incineration. Temperature gradient, residence time and gas velocity, as well as APC device sorption materials may affect the partitioning of metals between APC residue and stack gas, and it is therefore important not only to consider what APC system is employed but also how it is operated.

Table 12: Limits for, and analyses of stack gases emitted from a UK incinerator

metal	limit (2000/76/EC) (mg m^{-3}) (European Community Legislation, 2000c)	extractive test 1 (mg m^{-3}) (Fountain, 2002)	extractive test 2 (mg m^{-3}) (Fountain, 2002)
Hg	0.05	0.00014	0.00016
Sum of Cd + Tl	0.05	0.00047	0.00026
Sb	+	<0.00073	0.0041
As	+	<0.00073	<0.00074
Pb	+	0.0015	0.00074
Cr	+	0.0018	0.0048
Co	+	<0.00022	<0.00022
Cu	+	0.0058	0.00074
Mn	+	0.080	0.0020
Ni	+	0.0061	0.021
V	+	<0.00022	<0.00022
sum of all marked +	0.5	0.096	0.034

Complex Furnace Reactions, and Local Deviations from Bulk Conditions

It has been explained how the chemical and physical properties of a metal help to determine its partitioning, as do the associated incinerator and gas clean-up system conditions,. Therefore, a given metal will partition according to its own properties, and the incineration environment. However, there will also be many other metals undergoing the same processes simultaneously, and thus consideration of the holistic problem must be made. Examples of metal-metal interaction are observed in the displacement of sodium by potassium in aluminosilicates (Linak and Wendt, 1993), and by the competition of cadmium or lead with sodium for capture by sorbents (Davis et al., 2000). The importance of metal-metal interactions is indicated by the identification of species such as $NiCr_2O_4$ and $PbAl_2Si_2O_8$, which are seen to contain more than one metal, and are known to affect partitioning. It is extremely hard to assess the importance of such metal-metal interactions in the partitioning process, given the lack of data on the subject. However, it is important to remember such factors, if only as sources of additional information, when conventional explanations are observed to break down in practice.

Another aspect which has not been investigated in the literature, but which is likely to affect metal volatilisation, is the catalysis of reactions involving metals by co-present species or particles. Finally, it is important to remember that a mass-burn incinerator is a large, inhomogeneous process. Although bulk measurements of temperature, oxygen and acidic gas content are useful, they may not reflect conditions in all parts of the incinerator. Thus in local areas, the physical-chemical conditions experienced by a particular burning system may differ dramatically from those observed for the average of the whole system, so causing a deviation from expected behaviour, possibly having a significant impact on metal partitioning (Linak and Wendt, 1993, Yang et al., 2002, Wendt, 1994). It has already been shown how such local conditions, which are affected by the waste feed input, cause variations in organic pollutant emissions from

incineration of hazardous waste, and it is likely that inorganic pollutants follow similar patterns (Hart, 2001).

The physical – chemical environment of local areas of the burning bed, which may differ significantly from the bulk conditions, may be extremely important. They may cause local equilibria which are significantly different from the measured bulk properties, and so may lead to combustion products for metals which are not conventionally expected (Yang et al., 2002, Wendt, 1994). Various "exotic" metal species have been suggested as being important in metal partitioning, although in general chlorides, oxides, and possibly sulphates are considered to be the only major bulk components (Vogg et al., 1986, Abbas et al., 1996, Morf et al., 2000, Thipse and Dreizin, 2002). However, detailed predictions suggest the possible importance of species such as $Ni(CO)_4$, NiO_2H_2, CrO_2Cl_2, as well as reporting that other species, such as $PbCl_4$ may not to play as large a role as is conventionally expected. Mixed-metal compounds, such as $NiCr_2O_4$ are also reported, which may indicate the importance of the effect of one metal on the partitioning of another (Linak and Wendt, 1993).

Summary

It can be seen from the data presented above that modern incinerators are capable of producing gaseous emissions which are well below those considered by regulatory bodies to be acceptable. In addition, a bottom ash is produced, which is relatively inert, and the toxic components are mainly enriched in the APC residue. However, the factors affecting partitioning are many and complex, and are at best incompletely understood. In particular, the effect of local non-equilibrium conditions is thought to be important, but has not been investigated significantly experimentally. Thus improved knowledge of what factors affect metal partitioning, and how these factors can be manipulated may be important in optimising the incineration process. The next section will consider the behaviour of individual metals, looking at how they arise in the waste stream and at what concentration, how they behave during incineration, and why, for technical or toxicological reasons, their behaviour may be of significance.

2.3 Metals of Concern in Incineration: Their Partitioning, Toxicity (and Other Adverse Effects), Sources, and Major Uses

Given the vastly different properties of different metals and metal compounds, it is important to consider how significant these are in waste incineration and why. The subsequent section examines the properties of a number of metals individually, considering their partitioning between the different incinerator residues, sources in the waste stream, and negative effects in incineration products, in order to obtain an overview of why they give cause for concern in waste incineration.

It should be borne in mind that information provided may not be directly comparable, as it comes from a large number of different studies, which have employed different techniques. It is thus more important to examine general properties, than specific studies on particular metals. The availability of data on a particular metal generally reflects its toxicological, engineering, and ecological significance, with detailed studies on just one metal in some cases, and only fleeting incidental references to others.

The word toxicity means that a substance has an adverse effect on an organism (usually a human being). Although this sounds straightforward enough, complications immediately arise, and it is soon discovered that all substances, even the most benign, are toxic at high enough dose. Having identified some metals from combustion processes as being potential toxins, the cause of toxicity, and safe emission limit must be determined. The list of metals chosen for this work is based around those specified by both EU and US legislation, along with some of emerging, or technical rather than environmental or toxicological interest.

The first thing which is important to consider is how much exposure to a substance is to be considered safe. Some species are toxic at any measurable dose, whereas others need to be present over a threshold dose to cause an effect, the body being able to deal with trace amounts. Some toxins are rapidly broken down or excreted, whereas others accumulate in the body, meaning that long-term very low-level exposure can cause a significant effect.

A second, related aspect which is of is of importance is the duration of exposure. In the case of a fixed source, such as an incinerator, a fairly constant level of pollutant emission may be anticipated for a number of years, whereas some incidents, such as an accidental emission, may release a higher concentration of a substance for a shorter term. The "safe" exposure for a short period is likely to be higher than that for continued exposure, particularly for bio-accumulating toxins. Therefore, both short and long-term occupational exposure limits may be set, with different acute and chronic effects being observed for short and long-term exposure respectively.

The route of exposure (whether inhalation, ingestion, instillation, or absorption through the skin) determines uptake by an organism, and therefore the effect. Once a "toxic" species is in the body, the body tries to break it down and excrete it. Removal of small particulate matter from the lungs can be particularly problematic, leading to the concern about airborne pollution. Toxicity issues are further complicated by the fact that a substance itself may be non-toxic, while a break down product is.

The concept of synergy is most important when considering environmental toxins. Two toxins may be present at a below-toxic level, but if both affect the same biological pathway, then the combined dose may be above a safe threshold. In the case of metals, this may be particularly significant for those which are found in the body at a high oxidation state, causing oxidative stress to cells, where the effect of more than one oxidative stress will be cumulative.

Therefore, to classify a metal as being "toxic" is simplistic. The chemical form, oxidation state, and presence of aggravating compounds may all be significant, in addition to possible increased sensitivity of some population groups. Indeed, many metals have been shown to be essential, including Fe, Co, Cu, Cr, Mn, Mo, Na, Se, Sn, and Zn, but may still be toxic in sufficient quantity. Several are regulated in incinerator emissions, and it is to be assumed that emission limits are set on the basis of the best available information on optimum and harmful exposure. A good first indicator of the possible toxicity of a substance is the time weighted average (TWA) exposure limit for employees, as determined by the US occupational safety and health administration (OSHA), and these are given below for different metals. The average is for an eight hour average working day. These limits tend to be precautionary, being set low if there is a possible, but not fully understood effect, or if the specified material

may be a precursor to something more toxic (Goyer, 1996). Similar UK workforce exposure limits are also given (HSE, 2005).

Of course, when considering the toxicity arising from products of incineration, it is important to consider how abundant they are (naturally, and in specific applications and waste types), and how they behave in the incineration process, as this will control where they end up following incineration, and as a result what their effect on the environment or health may be. Section 2.2.2 examined what factors affect the distribution of different metals in incinerator residues, but did not consider the specific behaviour of different metals in detail.

There follows a brief indication of metal toxicity, along with uses, and behaviour during incineration (Table 13, Page 39). It must be emphasised that the information about metals and their common compounds should not be assumed to be exhaustive, but indicates why they are significant in waste incineration. Inclusion of a metal does not necessarily mean that it is of major environmental or toxicological concern, but may reflect its high abundance in nature and/or the waste stream.

Thus it can be seen that a great deal of information exists, on how metals occur in waste, behave in incinerators, and affect the biosphere if released in an uncontrolled manner. However, there are still significant gaps and inconsistencies in the information, particularly with respect to the incineration process itself. To achieve improved process understanding, accurate, and rapid techniques are required to analyse the metal-containing products from incineration, preferably on a time-resolved basis. The next two sections will consider the analysis of metals in waste and incinerator products, and will examine how these may be used to gain new information on how and why metals behave in the way that they do, while they are incinerated.

Table 13: The metals chosen for investigation, and some information on their toxicity and industrial significance

metal	notable industrial uses [1]	typical concentration in earths crust[2]	typical concentration in municipal waste [3]	volatility and partitioning behaviour during incineration [4]	comments on occurrence in waste and distribution	workforce exposure limit [5] *UK workplace exposure limit [6]*	comments on toxicology [7]
aluminium	Many and varied uses as alloy in construction, automotive, aeronautic etc.	8.2%		not volatile in combustion. ≥90% normally found in bottom ash	found significantly in "bulk" items in waste therefore inhomogeneous distribution	metal dust 5 mg m^{-3} *inhalable dusts, 10 mg m^{-3}, repairable dusts 4 mg m^{-3}, soluble salts 2 mg m^{-3}*	Toxicity from incineration not a major concern, but some forms can be toxic under specific conditions.
antimony	Alloys, batteries, semiconductors, flame retardants	0.2 ppm	10-60 ppm	significant volatility. 45-75% found in APC residue	Data on partitioning is inconsistent. Theory predicts higher volatility (Paoletti et al., 2001).	0.5 mg m^{-3} total Sb *As for US limit*	Known toxin, but not one of the most highly toxic metals.
arsenic	Specialist alloys, wood preservatives pyrotechnics, semiconductors	2.1 ppm	3-9 ppm	typically 70% of As found in bottom ash, although predicted volatility is higher	Expected to be more volatile (volatile compounds known). Slag formation on bed suspected.	0.05 mg m^{-3}, total inorganic As. *0.1 mg m^{-3} all As and As compounds*	Known carcinogen and toxin, with a low exposure limit as a result. Arsine regulated separately (lower limit).
cadmium	Electroplating, batteries, low-melting alloys, stabilisers in PVC (being phased out).	0.15 ppm	5-15 ppm	volatile, although figure varies between studies between 60-90%	Metal, oxide, and chloride all potentially volatile. Slag formation may reduce volatility. Thought to be very inhomogeneous in waste.	0.005 mg m^{-3} total Cd *0.025 mg m^{-3} for most Cd compounds*	Highly toxic, with multiple sites of effect. Bio-accumulating. Extremely low exposure limit as a result.
calcium	Cement, as a generic alkali in industrial processes	5.0%	1-3.5%	non volatile. ≥90% in bottom ash	distributed through a variety of wastes, mainly transferred to APC residue by entrainment	15 mg m^{-3} carbonate, sulphate, 5 mg m^{-3} hydroxide and oxide, *carbonate, 10 mg m^{-3} inhalable, 4 mg m^{-3} repairable, hydroxide 5 mg m^{-3}, oxide 2 mg m^{-3}*	Essential to life. High exposure limit reflects low toxicity. Some more harmful Ca compounds have lower limits.
chromium	Plating, alloys, hardening, wood preservatives, fungicides, catalysis.	140 ppm	40-400 ppm	non volatile. ≥95% in bottom ash	Some potentially volatile Cr compounds have been suggested, but seem not to be of major importance	Cr (III) 0.5 mg m^{-3}, Cr (VI) 0.05 mg m^{-3}, Cr (0) 1 mg m^{-3} *As for US limits, except Cr(0), 0.5 mg m^{-3}*	Cr (VI) highly toxic and carcinogenic. Other Cr oxidation states harmful, but of far less concern.
cobalt	ferrous alloys, colourant in ceramics and paints	30 ppm	3-4 ppm [7]	non volatile. ≥90% in bottom ash	very little data available	0.05 mg m^{-3}, total inorganic Co, *0.1 mg m^{-3}*	not of major concern as a toxin, although inhalation effects can be more severe
copper	widespread uses - electrical and electronic equipment, coinage, water pipes, construction, wood preservatives, insecticides, fungicides	68 ppm	200-1000 ppm	not significantly volatile in mass balance terms, ≥90% in bottom ash, but evidence of volatile transport available	CuCl and $CuCl_2$ thought to be important in the limited volatility seen. Form in which metal enters incinerator may be important (in bulk metal items, and distributed in combustible waste).	metal dust 1 mg m^{-3} *as for US limits*	An essential nutrient, but can be toxic at higher concentration. From incineration, not of major concern, although effects on lungs higher than via other exposure routes.
iron	extremely widespread – construction, automotive etc	6.3%	2.5-5.0%	non volatile. ≥95% in bottom ash	mainly found in "bulky items" in waste so inhomogeneous in waste stream	oxide, dust and fume 10 mg m^{-3} Fe, *iron oxide fume 5 mg m^{-3}, iron salts (as Fe), 1 mg m^{-3}*	Essential to life, not a major toxin. Reflected in high exposure limit.
lead	batteries, electronics, plumbing, ammunition, stabiliser in PVC (being replaced)	10 ppm	400-1000 ppm	volatile. 30-50% found in APC residue	Found in numerous applications, though being phased out. Metal, and its chloride may be important in volatility.	0.05 mg m^{-3} total inorganic Pb	A highly toxic metal, with multiple sites of action. Bio-accumulating. Reflected in low exposure limit.
magnesium		2.9 %	0.32 % [7]	non volatile. ≥90% in bottom ash	No suggested volatility. Transfer to APC residue is by entrainment.	10 mg m^{-3} for MgO *oxide, inhalable dust 10 mg m^{-3}, repairable dust 4 mg m^{-3}*	This is an American conference of government industrial hygienists (ACGIH) limit. OSHA has no limit, reflecting non-toxicity of this element.
manganese	alloys, batteries, matches, fireworks, porcelain	0.11%	200-500 ppm	non volatile. ≥90% in bottom ash	numerous sources in waste, notably batteries, where the MnO_2 powder may well be entrained	1 mg m^{-3} Mn fume, *Mn and its compounds, 0.5 mg m^{-3}*	Probably an essential nutrient, though toxic at higher concentration. Not of major toxicological concern normally.
mercury	Batteries, dental work, electronics (lamps) , laboratory equipment, pesticides. Being phased out.	0.067 ppm	0.5-5 ppm	Most volatile metal. ≥95% volatilised.	sources in waste should be diminishing, as use is discouraged	0.025 mg m^{-3} total inorganic Hg (ACGIH) 0.05 mg m^{-3} metal vapour *not listed*	Very low limits reflect extreme toxicity. Also bio-accumulates, and organic mercury which may form in environment, is even more toxic.
nickel	stainless alloys, coinage, catalysis, colourant in green glass	90 ppm	20-130 ppmp	Non volatile. ≥95% in bottom ash.	most forms of Ni in waste are in bulky items which limit release on burning bed	1 mg m^{-3} Ni metal 0.1 mg m^{-3} soluble Ni compounds *Water soluble 0.1 mg m^{-3}, water insoluble 0.5 mg m^{-3}*	Not highly toxic, but a major cause of contact dermatitis and therefore of environmental concern. Possibly carcinogenic.

metal	notable industrial uses [1]	typical concentration in earths crust[2]	typical concentration in municipal waste [3]	volatility and partitioning behaviour during incineration [4]	comments on occurrence in waste and distribution	workforce exposure limit [5] *UK workplace exposure limit* [6]	comments on toxicology [7]
potassium	biologically significant, used in fertilisers	1.5	0.5%	has significant volatility, with 20-30% found in APC residue	Chloride probably responsible for volatility. Widely distributed in waste. Important in boiler corrosion.	Short term limit of 2 mg m^{-3}. No long term limit. *no set limit*	essential to life, not of major concern as a toxin
silicon	Significant (essentially inert) component of geological structure of earth. Used in electronics, construction, glass making.	27%	3.7-3.8% [7]	Non volatile. ≥95% in bottom ash.	found largely in non-combustible wastes, largely unaffected by combustion process	most forms 6 – 10 mg m^{-3}, though some forms more highly regulated. *Most forms 10 mg m^{-3} total inhalable, 4 mg m^{-3} total repairable.*	not of toxicological concern in normal geological forms
sodium	Sodium salts have widespread uses, e.g. in paper, glass, soap, petroleum industries. Flavouring in food, essential to life.	2.3%	0.3 – 1.5%	Not very volatile, with >90% remaining in bottom ash. However, there is good evidence of volatile transfer routes.	Found in wide variety of wastes. Volatile in coal combustion, so probably volatile at higher waste combustion temperatures (chloride).	No limit for metal or general compound classification. Sodium bisulphate 5 mg m^{-3}, though specific compounds more regulated. *As for US limits.*	essential nutrient, not of toxicological concern in common forms
thallium	historical use as rodent poison, specialist glass products, semiconductors	0.53 ppm	0.2 ppm	Very scarce data. Appears to be non-volatile.	may participate in slag-forming reactions on burning bed	0.1 mg m^{-3} total soluble Tl (skin contact) *As for US limits.*	highly toxic, so common use is rare (compare concentration in rocks and waste)
tin	Metal plating, alloys. Significant in glass-making industry, historically used in biocides.	2.2 ppm	120 ppm	Significantly volatile. About 50% transfer to APC residue.	Widely used, mainly in alloys, plating and glasses. Chlorine probably important in volatility.	2 mg m^{-3} total inorganic Sn 0.1 mg m^{-3} organic tin *As for US limits.*	Tin in inorganic form not of major toxicological form, although organic forms (not thought to arise during incineration) highly toxic.
vanadium	Steel Alloys, catalysis	190 ppm	-	Very scarce data. Appears to be non-volatile.	mainly present in waste as alloys, in "non-accessible" form	No general limit for metal, though. V_2O_5 has short term limit of 0.05 mg m^{-3}.	respiratory effects seen from occupational exposure, but not an environmental toxin
zinc	alloys, galvanizing, batteries, paints, plastics, many other processes and products	79 ppm	600-2000 ppm	Significantly volatile. About 40-50% transfer to APC residue.	Very widely used, in both combustible and non-combustible wastes. Metal, chloride and oxide may be important in volatility.	Zinc oxide, 10 mg m^{-3}. Zinc chloride 1 mg m^{-3}. *Zinc distearate, 10 mg m^{-3}, inhalable dust, 4 mg m^{-3} repairable dust, zinc chloride fume, 1 mg m^{-3}*	Essential to life, and not conventionally considered toxic. However, some compounds (e.g. chloride) more harmful, as is inhalation exposure.

[1] (Winter, 1993, US National Safety Council, 2005)
[2] (Winter, 1993)
[3] (Van Der Sloot et al., 1997)
[4] (Linak and Wendt, 1993, Belevi and Moench, 2000a, Belevi and Moench, 2000b, Van Der Sloot et al., 1997)
[5] Limit set by the US occupational safety and health administration (OSHA), time weighted average for 8 hour working day (Goyer, 1996)
[6] (HSE, 2005)
[7] (Goyer, 1996, Nicolas and Descotes, 1996)
[8] (Belevi and Moench, 2000b)

2.4 Analysis for Metals in Municipal Solid Waste and Incineration Residues

Section 2.1.7 explained the need for analytical methods which allow the quantification of metals in the residues from incineration, and if possible in the waste itself, in order to identify the presence and partitioning characteristics of different metals in the incineration process. When selecting an analytical method, it is most important to remember what is trying to be achieved, and to choose a technique which is capable of meeting those requirements. Usually, as with most operations, there is a payoff between the absolute quality of the results, and the cost and complexity of achieving them. Thus questions which must usually be answered are (Fifield and Haines, 1995):

- What is the analyte: what needs detecting, and in what matrix?
- What concentrations of analyte are anticipated: thus what detection limits are required?
- What precision and accuracy are acceptable?
- What turn-around time for analysis is acceptable: is a continuous, on-line technique required?
- Are in-situ measurements required, or is laboratory analysis acceptable?
- Can the process be improved by automation, or are the techniques operator reliant, and therefore expensive?
- What capital costs and running costs are involved?

Any chemical analysis is essentially a modular system, comprising of a number of essential steps, as given below:

Sample Collection. A sample of the material to be analysed must be collected. The sample must be representative of the bulk of material being analysed.

Sample Pre-treatment. The sample may need to be altered in some way to prepare it for chemical analysis. For example, if the sample is solid, and the analytical technique used requires a liquid sample, then it must be fully dissolved. If the analyte is at very low concentration, it may need concentrating (e.g. by reducing the sample volume) to a level where it can be measured.

Instrumental Analysis. The prepared sample must be analysed for the species of interest. Usually, analysis must be both qualitative and quantitative or semi-quantitative.

For the analysis as a whole to be a success, each of these steps must be conducted in a satisfactory manner. Although sample collection may sound simple, obtaining a representative sample may be anything but straightforward, and ensuring that it is still representative when it reaches the analytical stage is even harder. Although pre-treatment is often essential, it must be done with care, to ensure that the level of analyte being analysed is, in fact, reflective of the concentration in the original sample. When the sample is then analysed, the analysis must be capable of measuring the species of interest (i.e. specific), at the concentration encountered (i.e. sufficiently sensitive), in the matrix encountered. Usually, the analysis must be quantitative, or at least semi-quantitative (i.e. giving a good approximation to the actual concentration found in the sample) (Fifield and Haines, 1995). By answering the questions posed above, it is possible to define which techniques (of sample collection, pre-treatment

and analysis) may be capable of achieving analysis to the required parameters. Having identified candidate techniques, an informed decision may be made on the basis of merits and drawbacks of different techniques (Fifield & Haines, 1995). However, in most cases, the first decision is the choice of instrument used, with the sample collection and pre-treatment techniques being optimised subsequently for the instrument which is being used for analysis.

For metals in municipal waste incineration, it is essential to know which metals (of those identified in section 2.3) are present, at what concentration. It is also desirable to know how concentrations vary with time, and what degree of homogeneity is observed in the samples taken. Some preliminary information on what values may be expected has been given in section 2.2.2. In order to obtain this, and further data, it is necessary to identify fundamental methods of unambiguously and quantitatively identifying multiple metals simultaneously, and consider how these techniques may be applied to the solids, liquids and gases which arise from waste and its incineration.

2.4.1 Analytical Instrumentation

Fundamental Detection Principles

In order to analyse a species effectively, a satisfactory detection technique must be found. In the case of metals, this means identifying some measurable parameter of that element which is specific to that one species, and which may be fairly readily detected. In terms of most basic chemistry, the atomic number of each element is unique, and so is characteristic of the element. However, it is not readily directly measured.

Mass Spectrometry

Linked to atomic number is atomic mass. Mass spectrometry is an established technique for determining the mass to charge ratio of species present in a sample which is ionised for analysis (Equation 1). Hence mass spectrometry can be used to determine atomic mass, provided that ionisation is controlled to minimise ionisations of more than one.

$$M + e^- \rightarrow M^+ + 2e^- \qquad (1)$$

Atomic mass can be used to identify elements, provided that resolution is high enough, and that there is not too much interference from other species which have the same nominal mass as the metal being analysed. Illustrative interferences encountered during metal analysis by low-resolution mass spectrometry are shown in Table 14. Methods are available to overcome such problems, but add to the complexity of the analysis (Beauchemin, 2002). Quantification is possible by mass spectrometry, as detection is by means of the electronic current generated by the ions produced. Ionisation is proportional to the concentration of a species present in the sample, and the current is then proportional to the number of ions (of a given mass) which are present.

Table 14: Possible interferences in mass spectrometry (Klinkenberg et al., 1997)

Mass	26	27	54	55
Species	^{26}Mg	^{27}Al	^{54}Fe	^{55}Mn
	$^{12}C^{14}N$	$^{12}C^{15}N$	^{54}Cr	$^{40}Ar^{15}N$
		$^{13}C^{14}N$	$^{40}Ar^{14}N$	

For mass spectrometry, various spectrometers may be used. These include Single focusing, double focusing, Ion-trap, quadrupole or time-of-flight mass spectrometers. Typically, selection is based on the cost, size, and resolution of the different detection systems, and the ease with which it may be coupled to different instruments. Mass spectrometry is inherently more sensitive than optical techniques, but suffers from instrument fouling if used with dirty samples. Its use is therefore generally restricted to trace determination in relatively clean samples (Willard et al., 1981). Therefore, the techniques are not the most straightforward to apply to highly contaminated samples from waste incineration, so they are not considered in further detail here.

Optical Emission and Absorption Techniques

The other broad detection category is by **electromagnetic interaction** of species with their environment. Electromagnetic radiation (e.g. light, infra-red or ultra-violet radiation) which interacts with matter becomes quantised, and provided that the energy of **absorbed or emitted light** can be measured accurately, this can be shown to be characteristic of the analyte. Both atoms and molecules can be analysed by such electromagnetic techniques, from low energy Nuclear Magnetic Resonance (NMR) spectroscopy, through to high energy Vacuum Ultra-Violet (VUV) spectrometry (Haines, 1995). The quantification of light which may interact with an atom occurs because of the behaviour of electrons in that element. These may only be at specific, discrete energy levels, and transfer of electrons between these levels requires the absorption or emission of specific quantities of energy, in the form of quantised electromagnetic waves.

The simplest and most familiar example of the quantisation of light interacting with matter is the flame test. It is why sodium salts make a flame burn with a bright orange colour, whereas copper salts cause the flame to turn blue-green. The most well-known and simple scientific study of the interaction of an element with electromagnetic radiation was with Hydrogen. Briefly, in 1885, Balmer discovered that the wave-number of the visible absorption lines of hydrogen were related (2). Further discoveries by Lyman, Paschen, and Rydberg led to the generalised formula (3):

$$\tilde{\nu} \propto \frac{1}{2^2} - \frac{1}{n^2} \qquad (2)$$

(where $\tilde{\nu}$ is the wavenumber (cm^{-1}), and n is an integer >2).

$$\tilde{\nu} = \Re_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \qquad (3)$$

(where $\Re_H$ is the Rydberg constant (=109677 cm^{-1}), $\tilde{\nu}$ is the wavenumber (cm^{-1}), n_1 is an integer, and $n_2 = n_1 + \geq 1$). This formula, and subsequently developed theory explains the quantisation of light which interacts with matter, and also why it differed for different elements (Atkins, 1994). It fully explains the observed spectra for elements, as shown in Figure 6 for hydrogen.

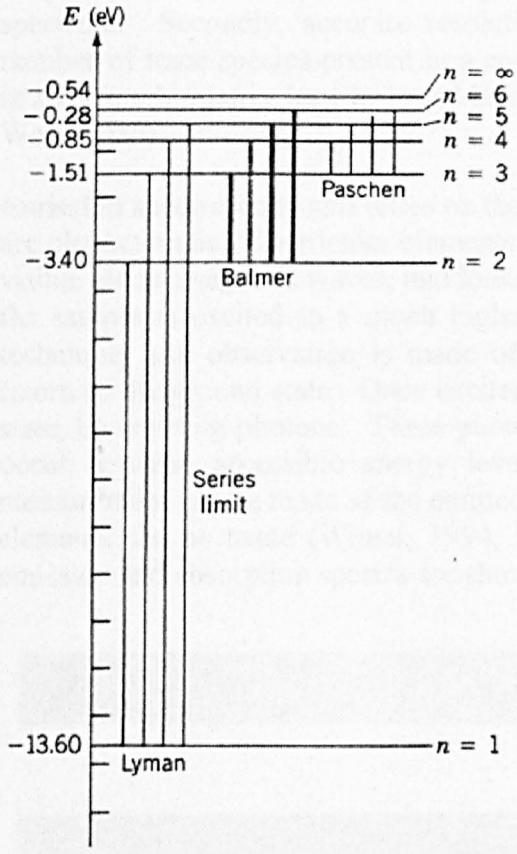


Figure 6: The hydrogen spectrum (Berg, 2003)

From early observations that the light absorbed or emitted by a species was characteristic of the elements it contained, irrespective of the molecules in which that element was found, the whole field of atomic spectrometry developed. Instrumental techniques have grown in complexity, and accuracy, speed, and quantification have all improved, but the underlying principles by which metals are identified remain the same.

For a complex system being analysed, there may be interferences at some wavelengths, where more than one element has an emission line at a similar value, making quantification difficult. However, optical techniques can still be used to identify all elements, as alternative lines may be found, because each element has far more than one transition line, as illustrated by Figure 6, which shows the transitions for the simplest element, hydrogen. More complex elements may have hundreds of transition lines (Haines, 1995). If an interference-free line cannot be found, modern instruments offer various computational corrections to improve measurements where spectral emissions overlap. For metallic elements, two types of **optical technique** dominate the analytical field; **absorption** and **emission spectrometry** of atomic or ionic species. Either technique aims to identify the characteristic transition wavelengths of an element of interest

Absorption spectroscopy involves exposing a sample to a broad range of wavelengths of electromagnetic radiation (a continuous spectrum such as a white light), and observing which are absorbed by the sample, causing excitation of the species to a higher energy level. This technique can work very well, but has some drawbacks. Firstly, it can be difficult to accurately measure absorption of one closely defined

frequency, when detectors are easily saturated by the remaining un-absorbed light spectrum. Secondly, accurate resolution can be difficult where there are a large number of trace species present in a complex sample, or when molecular constituents in the sample matrix lead to broad-band emission of light (Winter, 1994, Skoog and West, 1986).

Emission spectroscopy still relies on the detection of specific light wavelengths, which are characteristic of particular elements. However, instead of exposing the sample to visible electromagnetic waves, and looking for "absences" in the transmitted spectrum, the sample is excited to a much higher energy level, usually through an ionisation technique, and observation is made of the wavelengths emitted by species as they return to the ground state. Once excited, species loose energy to return to the ground state, by emitting photons. These photons are quantised because transitions can only occur between accessible energy levels of the species. Thus provided accurate measurement can be made of the emitted light, to a high resolution, identification of all elements can be made (Winter, 1994, Skoog and West, 1986). Typical continuous, emission and absorption spectra are shown in Figure 7.

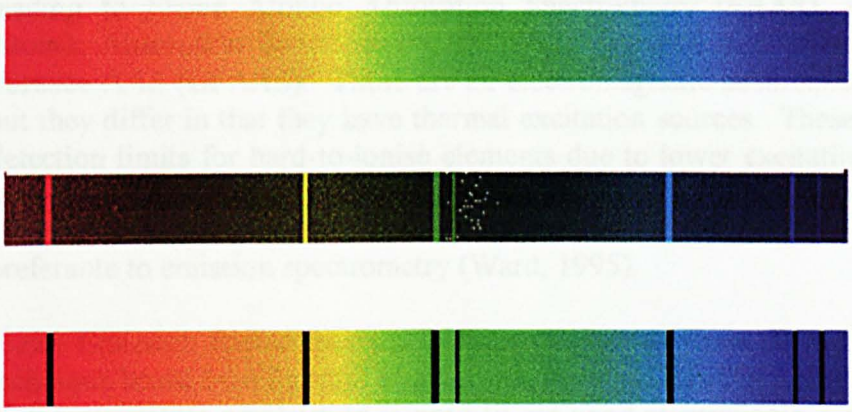


Figure 7: Continuous, emission and absorption spectra (Anonymous, 2003)

Once identification of a species is made, quantification of the analyte in the sample will be required. For emission spectroscopy, the intensity of emission can be measured electronically, and is proportional to the concentration of the species present, provided that the concentration does not exceed an upper detection limit, beyond which linearity is lost, due to saturation of the detector. Complex optical systems (diffraction gratings) are required to separate the emitted light into separate wavelengths, in order that detection of specific emissions can be measured separately. Recent advances in spectroscopy technology have been significant, and it is now possible to simultaneously detect and quantify a large number of different elements (typically around 40), taking advantage of complex detection systems that were not available previously (Skoog and West, 1986, Fifield and Haines, 1995).

Detection was first achieved using photo-multiplier tubes (PMT's). Diode arrays were then used, and now Charge-Coupled-Devices (CCD's) are available, offering all the advantages of solid-state electronics. In essence, the CCD is similar to that found in a digital camera. The advance of detector technologies has allowed simultaneous detection of multiple elements, rather than sequential detection (Fifield and Haines, 1995). The move from diode arrays to CCD's has also allowed an advance in background correction abilities, leading to reduced matrix effects (Hassaine et al.,

2001). The ability to record the whole analytical spectrum, which has been made possible through CCD detection is most useful in research and development applications, as it allows the user to confirm and re-quantify results after they have been collected, and examine spectral interferences in far more detail (Poole et al., 2005).

Different Instrumental Excitation Techniques.
If mass spectroscopy or emission spectrometry is to be used to identify metals in analytical samples, it is necessary to obtain excited atoms and ions, from which light and/or electrons is emitted. This requires that atoms in the sample become highly energised, and thus a source of excitation energy is required. Traditionally, this has been a thermal source, such as a flame or furnace although the field of instrumental chemical analysis has changed considerably in recent years due to the introduction of plasma-based excitation sources (Fifield and Haines, 1995, Thompson and Walsh, 1989).

Thermal Techniques.
Classical instrumental analysis techniques employed thermal excitation sources, leading to Flame Atomic Absorption Spectrometry (FAAS), and ElectroThermal Atomic Absorption Spectrometry (ETAAS), one example of which is the graphite Furnace AAS (GFAAS). These are all electromagnetic absorbance detection systems, but they differ in that they have thermal excitation sources. These tend to give poorer detection limits for hard-to-ionise elements due to lower excitation temperatures, and have the drawbacks of absorption over emission spectrometry which were outlined above. However, for relatively low energy excitation sources such as these, this is still preferable to emission spectrometry (Ward, 1995).

Flame Emission Spectrometry (FES), also known as flame photometry, is an emission technique based on a thermal source. However, a complex experimental set-up, using high temperature combustion is used to get good atomic/ionic emission from a flame source (Ward, 1995).

Through such techniques, sensitive, specific analysis of trace or ultra-trace concentrations of metals became possible. However, significant subsequent improvements became possible with the introduction of non-thermal excitation sources. Due to their higher excitation energies, these sources made mass spectroscopy techniques, as well as spectrometry techniques, available for the analysis of metals, as significant ionisation of analytes could be readily achieved.

Plasma Techniques.
A plasma is a "*...discharge in which densities of ions and electrons are high but substantially equal*"; a region in which a significant proportion of the species present are ionised (Tonks and Langmuir, 1929). In analytical chemistry a plasma can be a useful ionisation method, for mass spectrometry or emission spectroscopy (Mollah et al., 2000). The temperature in a plasma is typically in the region of 6000 - 8000°C, and ionisation of atoms is substantial, leading to strong emission signals for optical detection, or large numbers of ions for mass spectrometry. One drawback over cooler ion sources is that the increased emission makes line overlap in emission spectrometry (i.e. interference) more common. This problem may be overcome with higher resolution detectors, through selection of different emission lines, or through computational correction of interferences (Fifield and Haines, 1995).

Numerous methods have been used to generate plasmas, many of which can be used in an analytical context. The use of the popular Inductively Coupled Plasmas as ion sources for spectroscopy was first developed in 1964-5 (Greenfield, 1964, Wednt and Fassel, 1965). Since then, research into these techniques has been substantial, to the point where any regular review of any aspect of analytical chemistry will contain tens or hundreds of references to developments in the field of ICP techniques (Beauchemin, 2002).

The **Inductively Coupled Plasma (ICP)** is by far the most common plasma type in general analytical chemistry. A radio-frequency electromagnetic field is applied to a sample of gas, which becomes ionised as a result of the high energy density in the region. The plasma may be sustained in air, Helium or Argon (Baldwin et al., 1995, Gomes et al., 1997, Mollah et al., 2000), but most standard analytic techniques use an **Argon Plasma**, as the argon helps to maintain a stable plasma, and ionise the analytic sample, which is introduced into the middle of the plasma, and undergoes ionisation (Figure 8) (Fifield and Haines, 1995, Thompson and Walsh, 1989).

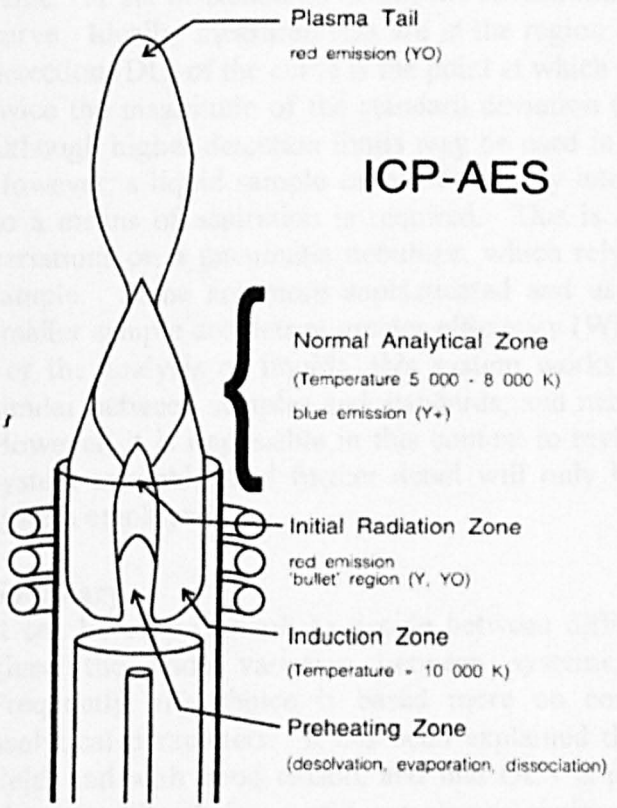


Figure 8: The ICP torch (Tyler and Horiba, 2000)

Depending on the analytical requirements, other plasma generators may be employed. The simplest is the **electric spark**, which causes ionisation through electric discharge. **Laser Induced Plasmas**, **Microwave Induced Plasmas,** and **Capacitively induced plasmas** have all been generated, and used for analytical purposes, but for general sensitive analytic work, none are as popular as the argon ICP (French et al., 2000, Meyer and Barnes, 1985). This tends to mean that although justification can be made for these other techniques for specific applications, the ICP is better for general work, purely because of the wealth of expertise available on their use.

Temporal stability and reliable ionisation are the characteristics which make argon ICP so popular. Laser and spark sources are pulsed, i.e. discontinuous, which makes spectral interpretation more difficult. In addition, these sources provide higher energy upon discharge, which can cause ionisations of greater than one, which adds to the complexity of the resultant spectrum (Fraser, 1999). The plasma volume created is smaller with these ionisation techniques, which means that ensuring the ionised sample is representative of the bulk is more difficult (Hunter et al., 2000), although in specific applications this can be an advantage (e.g. laser ablation allows the distribution of a metallic species throughout a solid sample to be determined to see whether surface and bulk properties are different (Beauchemin, 2002).

However, for general analytical work, the argon ICP appears to be the most useful method of generating ions. Those ions may be identified and quantified by mass spectrometry or optical spectroscopy, which are each discussed below.

Calibration Strategies.

In essence, whichever analytic system is chosen, the basic means of calibration is the same. A set of standards of known concentration are used to construct a calibration curve. Ideally, measurements are in the region of linearity of the curve. The limit of detection (DL) of the curve is the point at which an analyte signal is usually taken to be twice the magnitude of the standard deviation (SD) of the background (zero) signal, although higher detection limits may be used in more difficult analytical applications. However, a liquid sample cannot be readily introduced into an ion-generating region, so a means of aspiration is required. This is achieved with a nebuliser. Most are variations on a pneumatic nebuliser, which rely on the flow of a gas to aspirate the sample. Some are more sophisticated and use an ultrasonic vibration to generate smaller sample droplets at greater efficiency (Willard et al., 1981, Gomes et al., 1997). For the analysis of liquids, this system works well, provided the sample matrix is similar between samples and standards, and nebulisation efficiency remains constant. However, it is impossible in this context to review every nebulisation and calibration system available, and further detail will only be examined for the actual analytical system employed.

Summary

It can be very difficult to decide between different analytical techniques, especially given the wide variation between systems, depending on their optimisation. Frequently, the choice is based more on cost and availability than on absolute analytical parameters. It has been explained that ICP techniques now dominate the field, and with good reason, and that OES is preferable to MS, if OES is adequate. However, the choice is still not always obvious, and a summary of salient points of different systems is given in Table 15.

Table 15: A comparison of different analytical techniques

parameter	FAAS	ICP-OES	ICP-MS
initial Cost (£[1])	10 000 – 15 000	~ 50 000	110 000 – 115 000
running Costs[1]	low	medium	high
multi-element capability	separate measurements	simultaneous	simultaneous
overall advantages	good for general analysis of a limited number of analytes: robust, cheap	good for general sensitive analysis	good for trace and ultra trace analysis of "clean" samples
overall disadvantages	sensitivity, inability to measure multiple elements simultaneously	sensitivity for some elements and ultra-trace analytes	cost and stability

[1] **(Cox, 2002)**

For the analysis of metals in incinerator residues, ICP-OES was selected as the best overall analytical technique. Given the high concentrations of analyte expected, it was felt that the extra cost and complexity of a mass spectrometry system could not be justified, and there were also considerable concerns about the suitability and durability of a mass-spectroscopy based system for such contaminated samples. Plasma excitation was clearly advantageous for such samples, as the sample matrix is frequently difficult (amorphous, and variable), and an argon ICP was chosen. Given that it is among the most common techniques, within the field of advanced instrumental methods for metals, this was felt to be an advantage, because the technology was relatively robust, and the amount of information on system use was relatively high, which was felt to be an advantage for a research tool.

2.4.2 Sample Collection and Pre-Treatment for ICP-OES Detection

Conventionally, ICP-OES is used for the analysis of metals in liquid samples. Indeed, most standard analytical techniques for metals are designed to analyse liquids. As explained, incinerators produce solid residues, which usually require extensive pre-treatment prior to analysis, and gases, which require special sample collection procedures, as well as pre-treatment.

It should be noted that it is possible to analyse gases directly by ICP-OES, but techniques for doing this are experimental, being at the development stage still. Given the advantage identified in being able to sample incineration products continuously, gas analysis techniques for metals would be a great advance, as continuous monitoring of stack gas could be employed. However, this is a very specialist application of ICP-OES, and will be addressed separately in section 2.5. (Nore et al., 1993, French et al., 2000, Clarkson et al., 2003, Poole et al., 2005).

Liquid samples are therefore the easiest to analyse by ICP-OES. They may be analysed directly, possibly following dilution, or treatment (e.g. with acid) to break down complex structures in the sample matrix (e.g. suspended solids). Dilution may be required to ensure that the analyte concentration is within the range of linearity of the calibration curve of the instrument. (Fifield and Haines, 1995). Compared with solid residues, obtaining a representative sample of a liquid is relatively straightforward. However, given that incinerator operating conditions and waste feed change from day-to-day and week-to-week, it is difficult to assess whether a sample of water taken for analysis on a particular day is representative of that effluent stream all the time. However, because water samples mix well, and don't suffer from concentration gradients, it should be possible to obtain a sample of less than a litre, which is representative of the effluent stream at the time the sample is taken (Fifield and Haines, 1995, Van Der Sloot et al., 1997, Morf and Brunner, 1998).

Gaseous samples require trapping to be analysed in the liquid phase. This may be achieved using impinger solutions. Alternatively, a solid sorbent may be used to trap the gas, which is then treated as a solid sample (see below). Isokinetic sampling is employed to ensure representative particulate sampling, and heated sample lines are used to minimise condensation and deposition. Gases are usually difficult to sample, and the methods employed are complex, and difficult to accurately implement (Cooper, 1994, Clarke, 1998, Fifield and Haines, 1995). While it is possible to obtain a representative, isokinetic sample of flue gas for a particular monitoring period (typically of ½ hour to 8 hours), it is questionable whether that sample is representative of the gas stream, if such samples are only taken once or twice a year (Clarke, 1998, Poole et al., 2005, Van Der Sloot et al., 1997). However, at present this is considered to be the best way to measure metals, until continuous monitoring techniques become available (European Community Legislation, 2000a).

Solid Samples from incineration would tend to be highly inhomogeneous and so would lend themselves more to solution analysis than any of the solid analysis techniques, assuming that information is required on the bulk composition rather than on specific constituents of a particular incineration product. While samples are only taken infrequently, this is certainly the case. Usually, a strong mineral acid, or acid mixture (e.g. hydrofluoric acid, hydrochloric + nitric acid, perchloric acid mixture) is used to dissolve the sample. Remaining solids may have to be filtered off or compacted by centrifugation, but it must be borne in mind that some of the analyte will very possibly be lost in this way, particularly if the analyte is poorly soluble in the acid chosen. Ash samples can be dissolved and analysed in solution successfully, as can solid sorbents used to trap gaseous samples (Beauchemin, 2002, Ward, 1995).

For some analytes, a great deal of information can be gained by analysing samples directly as solids (e.g. by X-ray or neutron diffraction). Although these techniques are extremely powerful, and can give important information such as molecular arrangement and chemical speciation, they are not capable of routine quantitative analysis. For incinerator residues, and waste, the high sample inhomogeneity means that the sort of sample which may be analysed by such means is unlikely to be representative of the bulk material, and therefore these techniques are not reviewed further here (Fifield and Haines, 1995).

In order to obtain a representative sample of residue from an incinerator, or even of waste itself, extremely large samples are required, due to the fact that these streams are so inhomogeneous. For a detail study, several kg of APC dust would be required to be taken and mixed to a homogenous form. Similarly, for bottom ash, tens or hundreds of Kg are required, sampled periodically over an extended sample collection time. For waste, hundreds of Kg, or even tonnes may be required, again sampled for an extended period. Indeed, the problems of sampling waste are so great that it has been suggested that it is better to analyse the incineration residues, and calculate waste composition from this, rather than trying to analyse the waste itself (Belevi and Moench, 2000b, Morf and Brunner, 1998, Van Der Sloot et al., 1997).

Thus all the products of incineration may be presented for analysis, with varying degrees of ease depending on the sample matrix. Standard methods for the analysis of incinerator residues exist, based around the techniques discussed (British Standard 1756, 1971, British Standard 3405, 1983, British Standard EN13657:2001, 2001, US

EPA Standard 3050B, 1996, Reimann, 1989). Details of the methods which have been used for this work, which are based on these standard methods are given in Chapter 3 and Appendix 2. However, it has been seen that due to sampling problems, and the complexity of the sample preparation, these methods can only give incomplete information on metal behaviour during incineration. The methods for solid residues are unlikely to be able to give good time-resolved information on temporal variations in the process. Therefore, section 2.5 is dedicated to the examination of new continuous monitoring techniques, which may give further information on temporal variations in metal concentrations in gases, so providing new information on the incineration process.

2.5 On-Line analysis of Metals in Environmental Samples

As with any other field, environmental analytical chemistry is constantly developing. As analytical technology improves, as does any electronics-based technology, detection limits improve, analysis times are reduced, instrument cost and size are reduced, and resolution is improved. However, as well as these continual improvements, a step-change in analytical requirements is being observed. Historically, samples would be collected of a material of interest, such as an ash, soil, or process water, and would be returned to the laboratory for analysis, as explained for incineration samples in section 2.4. However, as environmental awareness has grown, and legislative requirements have become more rigorous, there has been a move towards the requirement for **Continuous, On-line, automated analysis** of process products.

Continuous monitoring is preferable, in that it allows real-time data acquisition (which may be linked to feedback control systems). Such data can be directly related to current process conditions, and specific problems or optimisations can be identified. Thus it can immediately be seen if there is a problem in a process, and as such if emissions are above set limits. In this case, corrective action can immediately be taken, provided that results are available rapidly enough. This is in contrast to traditional discrete sampling, where the results may take days or weeks to arrive, and when they do, they are time-averaged for the length of the monitoring period (as determined by the size of the sample collected). If the emissions are excessive or the product unsatisfactory, it is too late to alter the process, and modifications or improvement can only be made retrospectively. However, the advantages of on-line monitoring are accompanied by increased equipment complexity and cost, if indeed such equipment is available, although these may be offset by reduced sample preparation requirements and costs (Ward, 1995).

If metal emissions in incinerator residues were to be measured continuously, this would provide extra information for the regulators, and also information on plant operation, which would allow process optimisation. Sampling after the APC device would indicate stack emissions, and pre-APC measurement would give measurements which were indicative of the composition of APC residues. There would seem to be little interest in continuous measurement of bottom ash composition, which is probably technically near-impossible in any case, given its inhomogeneity, and difficulties associated with obtaining representative samples as a result (Reimann, 1989).

With modern analytical instrumentation, continuous monitoring of some sample streams may be quite straightforward. The analytical instrumentation is essentially the

same as that described in section 2.4, with relatively minor modifications of the sample introduction system for on-line analysis. A liquid sample can be pumped from the process to the analyser, and provided that extensive pre-treatment is not required, can be introduced as a standard liquid sample, with the instrument set to take multiple measurements (Spectro, 2005). Even homogeneous solids, such as steel samples, can be analysed in a completely automated manner (Kamphoff, 2004). Inhomogeneous solid samples are more problematic, although a solid analysis technique could in theory be used, or an automated dissolution system could be created. Laser ablation could be used to continuously introduce solid samples to an ICP, but there appears to be no literature references to the use of such techniques to samples of this nature.

Gaseous samples can be introduced continuously to a plasma, or indeed a plasma can be generated inside a duct carrying a gas. External plasmas require that an isokinetic sample of gas be pumped to the analyser, and this can lead to problems of deposition in the line, and so inaccurate sampling and analysis (Gomes et al., 1997, Seltzer, 2000). Frequently, the instrument itself will require modification to accept a gaseous sample stream. In-situ plasmas overcome this problem, but may suffer other problems, such as contamination or degradation of detection optics, or the intrinsic limitations of the type of technique applicable in this manner. Frequently, such instruments are custom-made for the purpose, so lack the flexibility afforded by using a standard analytical instrument (Woskov et al., 1996, French et al., 2000, Trassy, 1996). Nevertheless, for relatively clean and stable gas streams, accurate, sensitive monitoring of metals in gases can be achieved (Klinkenberg et al., 1997). However, the application of continuous monitoring techniques to the relatively difficult matrix of flue gas is still in the developmental stage, and is the focus of the following section.

2.5.1 Continuous Emissions Monitoring Technologies for Metals in Gases

Experimental Continuous Emissions Monitoring (CEM) techniques began appearing in the literature in the mid-1990's (Nore et al., 1993, Seltzer and Green, 1994, Peng et al., 1995). Previously, there had been very little by way of multi-element continuous monitoring which may have been applicable to gaseous emissions from industrial processes. The techniques applied to gaseous emissions, described in the literature, are inductively coupled plasma – mass spectrometry (ICP-MS), laser induced plasma/breakdown spectrometry (LIPS/LIBS), spark-induced breakdown spectroscopy (SIBS), Air inductively coupled plasma optical emission spectroscopy (Air-ICP-OES), and also Argon inductively coupled plasma – optical/Atomic emission spectrometry (Air-ICP-OES or Air-ICP-AES) (Klinkenberg et al., 1997, Flower et al., 1994, Fraser, 1999, Gomes et al., 1996, Meyer and Lee, 1994).

All these techniques rely on the formation of ions in a plasma. Optical Emission detection systems appear to be dominating the field, due to their lower cost (Gomes et al., 1997), although as shown above, there was little early consensus over the choice of plasma source. However, high water or CO_2 levels in the sample reduce sensitivity, due to the strong molecular absorptions of plasma breakdown products from these molecules, making the acquisition of good quality data non-trivial (Seltzer, 1998).

Since their first introduction to the literature, there has been significant interest in CEM techniques for flue gases, but little sustained research support, meaning that only one metals CEM is commercially available (French et al., 2000, Cooper, 2004). This unit is a quasi-continuous monitor, only producing 1 result about every 20 minutes. While this is a great advance for end-of-process regulatory monitoring, it does not

have the temporal resolution desired for combustion system investigation, where the aim would be to link output changes to process or input changes on a minute-by-minute basis. In section 2.5.2 the main components of a metals CEM will be described, and their function discussed. This will be followed by a review of the techniques developed so far, with an assessment of their suitability for the monitoring purposes described in this work.

2.5.2 Key System Components

The basic components of the metals CEM are the same, regardless of the actual analytical system involved; a continuous sample collection system, often with a sub-sampling system, a calibration system, an excitation source (plasma), a detection system (optical spectrometry or mass spectroscopy), and a computer control/data collection system. Wide variations are seen in how these components are realised, depending on other parts of the system and its specification. For example, sample lines between 1-40 m have been used, depending on the size of the detection unit, (and thus how remote it must be from the stack) and the availability of optical linking systems(Woskov et al., 1996, Gomes et al., 1997, Seltzer, 2000).

Sampling Line and Sub-Sampling System

For effective continuous monitoring, a system is required to transport the sample from the source (e.g. flue) to the analytical instrument. In the case of gases, isokinetic sampling is required, after which the sample is pumped continuously, at high temperature (above the dew-point of the gas or its components), to the analysis system (Clarke, 1998). In order to maintain sample integrity, and avoid particulate deposition in significantly contaminated gases, the tube diameter must be relatively large (8 - 14 mm), and so sampling volumes are large, in order to maintain velocity, which again is required for good particulate transport. For large, remote analysers, these sampling devices need to be of significant length. However, the volumes of gas transported from the stack are far too large to be introduced to an analytical instrument, and a sub-sampling system is required. This may either be a second stage of (near) isokinetic sampling, or may be based on a closed-loop sampling system. These sampling systems are difficult to design and operate successfully, and are often one of the largest sources of error in metals CEM (Trassy et al., 1997, Trassey, 2001, Clarke, 1998).

Sometimes, depending on the plasma type, the plasma may be produced in the gas stream being analysed, negating the need for a sample extraction system. For example, laser techniques may be operated in this way. However, optical linking to the detector system is required, and can be problematic. Generally, the additional design and robustness requirements of an in-situ device approximately balance out the advantages of an in-situ sampling system over an extractive sampling device, leading to similar sensitivities, stabilities, and drift etc (Woskov et al., 1996). Smaller, stack-based devices often suffer problems with inferior analytical systems, which do not match the performance of standard laboratory instruments, hosed further away (Timmermans et al., 2003, Trassy, 1996).

Calibration System

In the analysis of liquids, both the calibration standard solutions and the samples are introduced to the analyser by nebulisation, which produces a sample aerosol. However, for gases, calibration is less straightforward, as gaseous standards are effectively unavailable. The technique most commonly employed is to use a nebuliser and some sort of aerosol drying system to introduce aerosols of dry metal particulates

in order to calibrate the instrument. However, the method is subject to some criticism, as it is not clear how representative the calibration is of the actual sampling conditions. Careful characterisation of the nebuliser, and matching of the transport gas to the analyte gas is required (Gomes et al., 1997). Selection of an appropriate nebuliser, and optimisation of its operation, is most important, as nebulisation efficiencies can vary widely, leading to variations in instrument sensitivity (Seelig and Broekaert, 2001). Various other calibration methods have been tried, but this is by far the most established (Fraser, 1999, Trassy, 1996).

Excitation Source

Excitation sources in metals CEM are at least as varied as in conventional analysis (section 2.4.1) Further excitation sources such as microwave plasmas, lasers, and electric sparks have been suggested for stack monitoring. The main differences are in size and power, which dictates the size and remoteness of the monitoring system, and hence the sample collection requirements. Details of different plasma sources are given for individual techniques in section 2.5.3. However, for effective particulate and molecular gas excitation, a high power source is generally required (French et al., 2000, Trassy, 1996, Trassey, 1997).

Detection and Control System

As with excitation sources, the type of detection and control system used is widely variable. The control is now always PC-based. However, there does seem to be a significant quality difference between different detectors, with a noticeable difference in many cases between results obtained with commercial instruments, adapted for gas analysis, and with custom instruments, where the detection systems are often inferior (French et al., 2000, Trassy, 1996, Trassey, 1997, Timmermans et al., 2003, Woskov et al., 2000).

2.5.3 Existing Metals CEM Techniques – Key Features

Of course, the precise nature of the systems used depends on their intended purpose. Research based machines tend to be larger, and possibly less robust, whereas systems designed for eventual permanent installation in process plant may be more robust and cheaper, at the expense of giving less detailed and less sensitive measurement. A brief description of each of the published techniques is given in Table 16, with an overview of the relative merits of each, and their current status in the market.

2.5.4 Selection of a System for Metals CEM in a Municipal Waste Incinerator

Thus it is seen that many different systems, with different configurations have been investigated for metals monitoring in stack gases and other gases. For the current work, argon ICP-OES was selected as the most appropriate technique, due to its established use in metals analysis and the resulting amount of information available on the technique, the flexibility of the system (i.e. a commercial instrument), and the good detection limits seen from ICP-OES in stack gases (French et al., 2000). Full details of our specific system are given in Chapter 3.

Table 16: Comparison of different metals CEM techniques

system	extractive or in-situ measurement?	key features / details	capital cost	typical detection limits(mg m^{-3})	history	Selected references
Ar-ICP-OES (US group)	extractive	Established ICP instrumentation. Biggest weaknesses sample line (possible deposition?) and sample interface (closed loop or virtual impactor).	moderate	0.005-0.0001	Developed mid-late '90s. Less published work recently, understood not to be under active development.	(Seltzer, 2000, Seltzer and Meyer, 1997, Meyer and Lee, 1994, Meyer, 1991)
Ar-ICP-OES (French group)	extractive	Established ICP instrumentation. Sampling and calibration still the biggest issues. Seems now to be an entirely laboratory-based system.	moderate	0.01-0.0002	Developed mid-late '90s, from air-ICP initial work. Tool now in use for laboratory furnace investigation. Good quality publications relatively often. **Still Active.**	(Trassy and Diemaizonek, 1994, Trassey, 1997, Trassy, 1996, Abanades et al., 2001, Abanades et al., 2003)
air-ICP-OES (US group)	stack-mounted extractive	improved running costs (no argon), fair detection limits, advantages of in-situ technique (less sampling issues)	moderate	Not available	Developed mid-late '90's. No recent publications, assumed to be abandoned at present.	Reported in (French et al., 2000)
air-ICP-OES (French group)	extractive	improved running costs (no argon), some sensitivity issues		0.01-0.001	Developed mid-late '90's. No recent publications, assumed to be abandoned at present.	(Gomes et al., 1998, Gomes et al., 1996, Nore et al., 1993)
Ar-MIP-AES	stack-mounted extractive, could be in-situ	potentially very good, but some sensitivity issues	moderate	0.1-0.001	Developed mid-late '90's. No recent publications, assumed to be abandoned at present.	(Woskov et al., 1999, Woskov et al., 1996)
air-MIP-OES	extractive	potentially good, but only demonstrated in the laboratory to date	moderate	0.0004-0.0029 in lab conditions	Developed late 1990's. No publications since 2001, assumed to be abandoned at resent.	(Seelig and Broekaert, 2001)
laser induced breakdown / plasma spectroscopy (LIBS/LIPS)	in-situ, laboratory tests extractive	Most developed in-situ technique. Some detection limit issues. Of interest as in-situ technique. Calibration issues remain.	high at present but potentially competitive	0.4-0.002 0.0001-0.06	Continued development mid-1990's onwards. No information on current developments since 2001. Most prolific CEM publishers over a sustained period.	(Flower et al., 1994, Peng et al., 1995, French et al., 2000, Zhang et al., 1999, Zhang et al., 2001b, Buckley et al., 2000)
laser induced breakdown / plasma spectroscopy (LIBS/LIPS)	extractive at present, but could be in-situ	only demonstrated in laboratory so far, limited range of elements investigated	presumed to be potentially competitive	0.4-0.002	first publication 1994, most recent 2000	
spark induced breakdown / plasma spectroscopy (SIBS/SIPS)	in-situ	In situ monitoring device, therefore of interest. Suffers detection limit problems. Running costs could be low.	lower	0.001-0.1	Developed mid-late '90's. No publications for air monitoring since 2001. assumed to be abandoned at present.	(Fraser, 1999, Fraser et al., 2000, Hunter et al., 2000)
MIP-OES	near-stack extractive	Minimises the problems of sample transport by being near stack. However, detection system leaves much to be desired. Interesting as only group to attempt to measure contaminated (pre clean-up) stack gas.	moderate	not given, but stated to be poor compared with Ar-ICP techniques	First paper published in 2003, therefore assumed to be **still active**. Thus of interest as unique in examination of contaminated gas.	(Timmermans et al., 2003)
ICP-MS (speculative characteristics for flue gas monitoring)	extractive	highest sensitivity available if required	high	demonstrated to be <0.001 ng m^{-3} in some case	has not been applied to stack monitoring, but shown good potential elsewhere	(Klinkenberg et al., 1997)
X-ray diffraction of depositions collected on a filter	extractive	Automated system giving a result every 20m or so. Commercially available, understood to be expecting regulatory endorsement soon. Uses commercial XRF. Time resolution not suitable for system variation investigations in MSW incineration.	will be competitive if sold in volume	less than required limits, not given specifically	under commercial development for many years (1990's), but very few literature publications	(Cooper, 1994, Cooper, 2004)

2.6 Theoretical Prediction of Metal Behaviour in Thermal Systems

The aim of modelling the behaviour of metal compounds in incinerators is to determine where the metals entering the incinerator leave the incinerator, either in the bottom ash, APC residue, or flue gas. Having seen how important this is, in terms of the incineration process, its environmental impact, it should be clear why an improved theoretical understanding of how metals behave in such systems is important. Following initial experimental investigations of metal partitioning, many studies have attempted to model the behaviour of metals in incinerators and other combustion systems, with varying degrees of success, and using different modelling techniques (Brunner and Monch, 1986, Linak and Wendt, 1993, Barton et al., 1990, Lockwood and Yousif, 2000). Essentially there are two main approaches to this task, as explained below:

In thermodynamic equilibrium modelling, it is assumed that all the components in the fuel are exposed to the conditions found in the combustion system, and reach full thermodynamic equilibrium with one another, yielding solid, liquid, and vapour products (Delay et al., 2001, Wu and Biswas, 1993). Both pure species and mixtures (slags and melts) may be obtained. The volatility of different products determines which species leaves the furnace as a vapour (which is captured in the APC device, or emitted with stack gas), or are retained in the solid (bottom ash). These studies not only give indications of the species which are important in metal transport, but can also indicate which system variables (e.g. plant temperature, chlorine concentration in waste) may have a significant effect on metal distribution (Wu et al., 1994). However, if they are solely thermodynamic in nature, they cannot account for entrainment, which is also important in metal transport.

A second equilibrium calculation can be performed for the gas cooling in the APC system, for those species transferred to the gas phase, to determine whether they are trapped by the APC devices as the temperature falls, or whether they are emitted to atmosphere. In such a calculation, it could be assumed that all condensed species were captured by an efficient APC. Theoretically, a thermodynamic calculation could be applied to a lime or activated carbon scrubber system, but this does not appear to have been done to date.

The other main approach is to use aerosol dynamics to predict what will happen to metal vapours, or airborne particulates, which are carried from the furnace in the flue gas stream. Some information on particulate transport was given in section 2.2.2. Nucleation, condensation, coagulation and deposition are described mathematically, and these calculations are used to predict what will happen to the aerosol size distribution by the time it reaches the APC device. Capture by the APC device is based on the size of particles in the aerosol, as the capture efficiencies for different (non-reactive) particles are relatively well known (Lockwood and Yousif, 2000, Wu et al., 1994). These models identify the need to incorporate more thermodynamic and reactivity data, to improve model accuracy. The other major limitation of aerosol dynamic models is that they only apply to evaporative transport mechanisms, and do not account for entrained material, even though aerosol dynamics ought to be able to describe entrainment.

Initially, models fell into one of these two distinct categories, either using theories of aerosol dynamics, or of thermodynamic equilibrium. However, more sophisticated recent models began to integrate the two techniques, using thermodynamic predictions

to assess which metals leave the combustion chamber with the stack gas, and using aerosol dynamics to predict the fate of these compounds on their course through the incinerator (Barton et al., 1990, Wu et al., 1994). Such models evidently have more potential to describe the partitioning of different metals overall, but to date, such methods have been limited in their success, often requiring extensive empirical correction, due to the limitations of the underlying modelling approaches.

Ideally, the aim of modelling metal behaviour in a combustion system would be to produce a fully descriptive kinetic model, of how and why any metal behaves the way it does in the system. Numerous reactions would have to be considered in terms of equilibrium and kinetics, and aerosol dynamics would have to be calculated in full. However, the input data requirements (in terms of the fuel, and the process), would be extremely significant, and any results would be highly specific to a particular plant working under specific conditions. Work on a simplified kinetic model of this nature has been begun for mercury (Sliger et al., 2000). Although still under development, this technique shows very promising initial results.

However, a major problem of increasing model complexity is the data availability, both to create the model, and as an input for the model, if it is to account for variations in the process. In fact, this is often the main problem with any of the modelling approaches when applied to MSWI. Information on the waste feed, or the nature of the combustion on the burning bed, is simply not known to the required accuracy. Even if it were, such values would be subject to change with combustion conditions to a degree where the modelled results would vary unacceptably, given the range of operating conditions which may normally be encountered, unless the model was run for multiple combustion conditions, according to the data obtained on the combustion process at a given time. Thus the need for improved modelling techniques is always balanced by the need for better information on the incineration process on which the model can be founded.

The verification of the accuracy of models can also be a problem. This is especially true for MSWI, where the input waste is particularly poorly characterised. In contrast, models for coal or hazardous waste incineration, where the input composition is better known, have been more verifiable (Linak and Wendt, 1993, Delay et al., 2001). For a waste stream as diverse and inhomogeneous as municipal waste, it is doubtful whether any model could ever be fully quantitative and fully predictive of residue compositions, unless it was an on-line model, which was able to re-calculate results on the basis of the waste input (which would need to be well known), and the combustion conditions, on minute-by-minute basis. Nevertheless, the models which are available allow us to gain an improved understanding of how physical and chemical parameters determine metal partitioning, and investigate theoretically how changing processes can change metal behaviour. This has already been seen to some extent for particle behaviour in section 2.2.2 (Delay et al., 2001, Yousif et al., 1998). This section reviews existing information on the techniques available, and what they tell us about the combustion process.

2.6.1 Thermodynamic Modelling

In this technique, all the components in the waste are considered to be in equilibrium with one another, and predictions are made as to which species are formed, and at what concentration for all the elements considered. The volatility of these predicted products is used to judge whether these will then partition into the bottom ash, or be

carried in the gas phase through the incinerator. These models can be extremely useful, as they consider what species may form, and which are important in determining metal volatility or non-volatility (Fernandez et al., 1992).

Underlying Principles

The thermodynamic principles involved are essentially simple. Any reactant mixture is in equilibrium with any possible reaction products, at any given temperature. Reaction will occur if enthalpy of formation (reaction) is exceeded, and a mixture of starting materials and products will result. The equilibrium point is dependent on the thermodynamics of the possible reactions, and on the heat capacities of the products (Atkins, 1994):

$$\Delta G = \Delta H - T\Delta S \quad (4)$$

(where G is the Gibbs free energy (J mol^{-1}), H is the enthalpy (J mol^{-1}), T is the temperature (K), and S is the entropy (J K^{-1} mol^{-1})

and

$$\Delta G = -RT \ln K \quad (5)$$

(where G is the Gibbs free energy (J mol^{-1}), R is the gas constant (8.31451 J $K^{-1}mol^{-1}$), T is the temperature (K), and K is the equilibrium constant (no units), which is dependent on the quotient of the reaction products and the reaction starting materials).

These two basic physical equations can be used to predict the equilibrium distribution between a set of reactants and products at a given temperature, through minimisation of the Gibbs free energy, provided that the necessary physical data is available for all the compounds concerned. For a simple reaction, with a limited number of reactants and products, such as the reaction between a metal and oxygen, calculation of the global energy minimum is simple. Essentially, the question to be answered is whether the metal or its oxide is more stable at the temperature and oxygen concentration being considered, and if an oxide, then which oxidation state.

In essence, the principle of the prediction gets no more complex than this, but actual calculation increases dramatically, as further reactants and possible products are introduced, especially when non-binary systems are considered, (e.g. those where there are more than one metal which may react with an anion, and where more than one anion is available to react with each metal). In these situations, actually describing a problem which may be solved can be challenging, and the computational requirements for a solution can be significant. In many cases, the data requirements for accurate calculation are substantial, and much of the data has to be assumed or approximated (Argent, 2004). Further details of the computational method actually used are given in Chapter 4.

Literature developments of Thermodynamic Modelling techniques

One of the first attempts at thermodynamic prediction of possible reactions in a MSW incinerator was in 1988 (Lee, 1988). Unusually, this work casts governing equations in the form of chemical potentials, rather than Gibbs free energy, for their own convenience, but this in no way affects the results obtained. The model is useful from

an illustrative point of view, but the detail is subject to some criticism, as it considers insufficient reacting species, most notably for slagging reactions, which tend to increase the proportion of volatile metal which is retained in the bottom ash(Paoletti et al., 2000, Delay et al., 2001). Significant improvements have been made in the data available for such modelling in the intervening years (Argent, 2004).

Nevertheless, early predictions for Hg, Pb, & Cr are obtained. It is predicted that 100% of mercury and lead entering the furnace leave as vapour, in all of the operating conditions considered. The high transfer to gas phase reflects the lack of consideration of slagging reactions. However, the important combustion variables of temperature, chlorine concentration and excess air are identified and considered, though not simultaneously, due to the limitations of the computations available at that time (Lee, 1988).

The initial work by Lee on thermodynamic predictions of metal behaviour in incinerators was based on a wealth of similar information obtained about other systems, most notably the thermodynamics of the behaviour of trace elements in coal combustion and other "hot" processes. Thus the work had a good basis, with considerable expertise being available on the technique. It was followed by work which sought to rationalise observed experimental data on the composition of incinerator residues by using thermodynamic predictions (Fernandez et al., 1992). The work essentially uses thermodynamics to answer the question "if I see a product in the fly ash, how did it get there – as metal, as chloride, or as oxide?" by considering which of these species are thermodynamically possible, and is a very useful approach, given the known constraints on modelling waste combustion, given the inhomogeniety of the system (Linak and Wendt, 1993).

In some cases, the full range of necessary compounds involved in metal partitioning are not considered, in particular metal-metal interactions are not included, and there is evidence that a lack of appropriate thermodynamic data is the reason for this. Specifically, the work does not consider bottom ash "complexing" reactions through slag formation, nor the role of sulphur in suppressing volatility. The work gives a good thermodynamic rationale for fly ash / gas partitioning in terms of APC device temperature and metal chloride volatility. These thermodynamic predictions could be seen as an "upper limit" of metal transfer to the fly ash and gas phases, as most of the reactions which enhance volatility are included, but those which may suppress it are not (Lee, 1988).

A more recent review gives some examples of equilibrium calculations in waste combustion systems, which are essentially similar to those already described, but with somewhat better consideration of "competing reaction products", i.e. the reaction of metals with sulphur, which tends to depress volatility, as well as with chlorine, which is usually considered as it tends to enhance volatility (Linak and Wendt, 1993). Further equilibrium analysis of waste incineration was attempted in the same year, but the results contribute little more to the knowledge about such combustion systems, due presumably to limitations in the data available, and computational power (Wu and Biswas, 1993). More recent work on clinical waste incineration has shown a far more sophisticated approach to the calculation, reflecting the improved techniques available, but is not directly applicable to municipal waste, due to the differing input composition and incineration technology (Delay et al., 2001). Nevertheless, it demonstrates the

improvements which could be made to available modelled results, with the advantage of modern thermodynamics packages and computers.

Limitations of thermodynamic modelling

Although the early work on thermodynamic prediction of metal partitioning is generally excellent, it also demonstrates well the difficulties generally encountered with the technique. Firstly, there is an incomplete availability of data on the thermodynamics of all the reactions which may be significant, and the computational techniques may not allow the simultaneous inclusion of all the species required. The second problem is the inherent one: that the assumption of equilibrium is reasonable in a municipal incinerator. Clearly, this is a significant assumption for a large and heterogeneous system such as a municipal waste incinerator. (Linak and Wendt, 1993, Delay et al., 2001). A more detailed consideration of these limitations is given in Chapter 4, along with consideration of how these difficulties can be minimised.

Summary

It has been shown that thermodynamic modelling is a well established technique, developed for use in other industrial processes, but applicable to MSW incineration. The value of the technique has been shown in the modelling of waste incineration systems, provided that the "problem" (modelled situation) can be adequately described, and that the relevant data to define the problem is available. Although there has been significant work already in modelling municipal waste incineration systems, there is also considerable room for improvement, through use of better input data, and use of the newest computer programmes, which allow a more comprehensive consideration of the "whole system" equilibrium. As will be seen below, the use of thermodynamic modelling is probably the best available technique for estimating transfer of metals to the gas or particulate phase, as a means of generating input data for aerosol dynamics modelling. Possible methods of overcoming the problems identified with the assumption of global equilibrium, and specific application of the technique to MSW incineration are considered in detail in Chapter 4.

2.6.2 Aerosol Dynamics modelling

The fundamental basis of aerosol dynamics is extremely simple. An aerosol is a collection of liquid or solid particles in a gas. For incineration, the aerosol is generated in the burning bed, through evaporation and entrainment, and develops as it passes through the incineration system. Aerosols change through condensation, coagulation, and deposition, as well as through particle generation, and in the case of an incinerator, these processes all occur between the burning bed and the APC device, which serves to remove nearly all of the solids and liquids from the aerosol at the end of the incineration process.

The mathematics of aerosol dynamics are very well understood on a theoretical basis, (Friedlander, 1977). This book is the fundamental reference source for most subsequent computational modelling involving particle dynamics, although modifications to the theory may be required for specific situations (Lockwood and Yousif, 2000). The mathematics involved is extremely complicated in some parts, but appears to work well, if appropriate input parameters can be measured or estimated. Once again, the data requirements are demanding, and this provides particular problems for poorly characterised combustion beds used for MSWI. Indeed, even for relatively well characterised flames from pulverised fuels, it is the availability of data which limits the use of such models (Lockwood et al., 1998). The full details of the

mathematics are not included here, as it is largely incorporated into existing commercially available modelling programmes, and so a general overview only is given (Linak and Wendt, 1993).

The main group to investigate the use of aerosol dynamic models in combustion systems have generally avoided municipal waste combustion, presumably because of the complexity of the problem. Despite a proliferation of high quality papers on other combustion systems, their avoidance of municipal waste suggests that this technique may not be the best for rationalising the behaviour of municipal waste during combustion (Lockwood et al., 1998, Yousif et al., 1998, Lockwood and Yousif, 2000, Dajnak et al., 2003)

It would appear that they have done more work on the condensation of particular metals (Cd, Pb, Hg), to refine the models according to improved knowledge of these processes. However, their work is on better defined fuels, such as sewage sludge and coal, so the problem of unknown input is less significant. Thus the direct transfer of their work to an MSWI could be extremely problematic, as it is has concentrated more on obtaining accurate results for a specific situation, rather than obtaining a generally acceptable model.

However, at a conceptual level, much of the work by the group is extremely relevant. Their refinement of the model with consideration of slagging reactions, and of the form of metal entering the combustion system (carbonate//organically bound) is both sensible and useful. Most of the aerosol modelling is simplified by considering a bimodal PSD of just two sizes (<0.5μm and >10μm), which while being a significant assumption, seems to be a reasonable simplification of the problem, and which appears to work in practice!

The group uses a small scale test furnace for its work, so all the models are well verified against experimental evidence, though the agreement between the results is not always ideal.

The majority of the work by the group used essentially the same aerosol dynamic principles. However, they seem to have progressed a long way in the areas of empirical model refinement and verification for particular metals, leading to very good agreement between modelled and observed behaviour, as shown in Table 17. Rather than describe in detail their refinements in this literature review, such information will be included in subsequent model development as and when required.

Table 17: Agreement between modelled and measured enrichment of heavy metals in submicron particles from coal combustion (Yousif et al., 1998)

metal	experimental value	predicted value
cadmium	22.3	20.12
lead	11.6	10.03

Underlying Mathematics

A General Dynamic Equation (GDE), also known as the Convective diffusion mass balance equation is described, and is seen to be common to many of the modelling techniques described subsequently (Linak and Wendt, 1993):

$$\frac{\partial n(x,t)}{\partial t} + \nabla . n(x,t)v = \nabla . D\nabla n(x,t) - \nabla nc + R_v (m^{-3}s^{-1}) \quad (6)$$

where n is the particle number size distribution term (m^{-3}), and the equation describes the number of particles per unit volume in the particle volume range v to v+dv at position x and time t.

υ is the gas velocity (ms^{-1}), D is the diffusion coefficient (m^2s^{-1}), c is the particle migration velocity resulting from external forces including gravity (ms^{-1}), R_v is the particle source term ($m^{-3}s^{-1}$) (at position x and time t).

This general equation describes the spatial and temporal evolution of a PSD function n(v,x,t) (number of particles n in the particle volume range v to v+1, with convective and diffusive terms. Internal processes alter the nature of the aerosol cloud, i.e. coagulation, condensation and nucleation affect particle density and size distribution, so these must be accounted for.

Thus the source of particles, R_v, comprises of 3 terms, describing coagulation (R_{coag}) ($m^{-3}s^{-1}$), condensation (R_{cond}) ($m^{-3}s^{-1}$), and nucleation (R_{nuc}) ($m^{-3}s^{-1}$):

$$R_v = R_{coag} + R_{cond} + R_{nuc} \quad (7)$$

Further equations are given in the paper for the generation of each term, though these are not repeated here. They are based on well established aerosol dynamic principles (Friedlander, 1977). The result is the generation of an aerosol of particles which is well defined. Number density considerations then explain the observed enrichment of volatile metals on the surface of smaller particles, which have a far higher number density. The aerosol particle size distribution (PSD) evolves with time, as particles coalesce and drop out of the gas stream.

2.6.3 Combined models for specific applications

Having seen that both thermodynamic and aerosol dynamic models can be extremely powerful tools in explaining and predicting metal behaviour in combustion systems, but that they also have significant drawbacks, it is interesting to consider how these models may be combined. A multi-part model, incorporating a thermodynamic model and a aerosol dynamic model, was produced as shown in Figure 9 (Barton et al., 1990). It was designed for hazardous waste modelling, so significant changes would probably be required for its successful application to MSWI, but it illustrates how combined models can overcome some of the limitations of individual techniques.

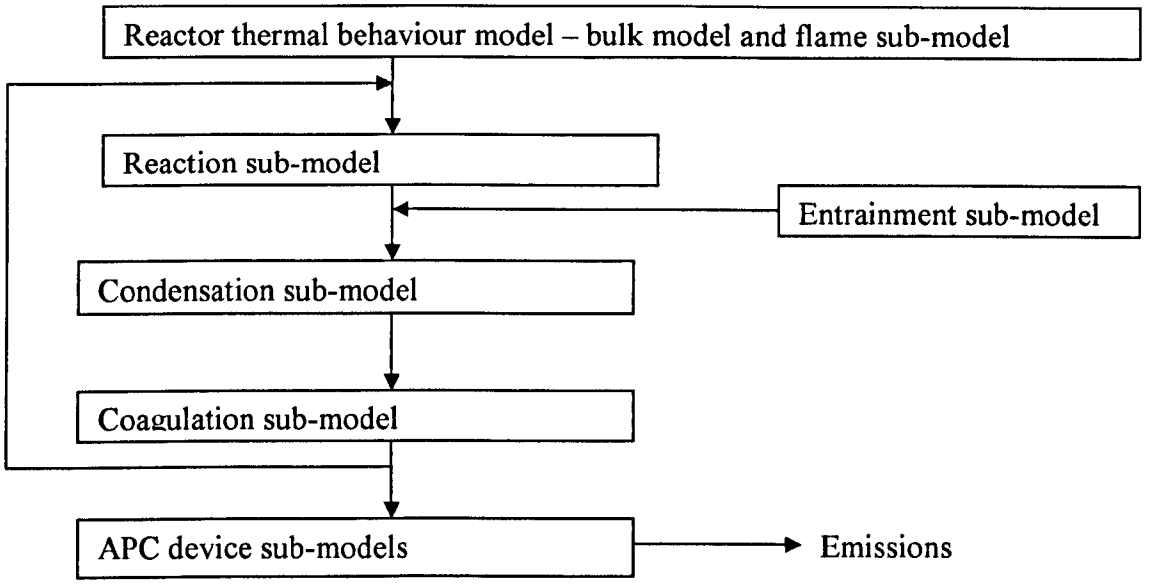


Figure 9: The Sub-Models Involved in the Aerosol Dynamic Modelling of a Hazardous Waste Incinerator (Barton et al., 1990)

The thermal model is empirical, and describes the changing temperature profile on the bed. The reaction/phase behaviour model is based upon thermodynamic equilibrium. Although little detail is given of the actual thermodynamic model, although it is assumed to be generally similar to the approaches already outlined, and may cause significant error, given the known non-equilibrium tendencies of such combustion systems. The entrainment model is again empirical, being specially devised for this model.

The fundamental model comprises of two parts. Homogeneous condensation modelling is based on the classical Becker-Doring theory, and homogeneous condensation is based on the kinetic theory of gases. This equation applies for particles much smaller than the mean free path of the gas, which is typically 0.25 μm in an HW incinerator, and so significant error may be introduced here (Friedlander, 1977, Barton et al., 1990).

Another group has worked on a combined thermodynamic and aerosol dynamic modelling approach (Wu et al., 1994). They produced a limited thermodynamic equilibrium and mass transfer based model with limited success and considerable room for improvement. It contained several empirical corrections for un-explained phenomena and was compared with potentially questionable raw data. It was, however, one of the first papers to apply such a combined modelling technique to a MSWI, so is significant for that reason. A schematic overview of the modelling strategy is shown in Figure 10.

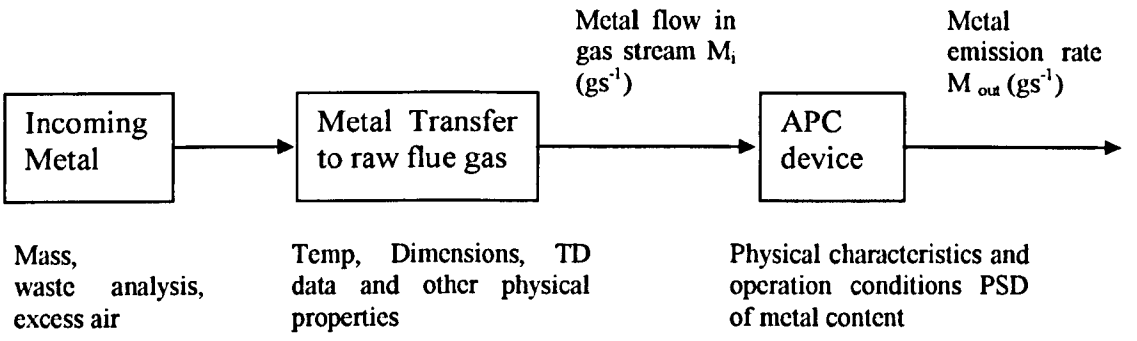


Figure 10: The components of a combined thermodynamic and mass transfer model of MSW incineration.

Mass transfer is described by the equation:

$$M_I = (0.037 \mathrm{Re}_L^{0.8} Sc_i^{0.6} D_i W C_{sat,i}) f_i = m_{th,i} f_i \quad (8)$$

Where Re = Reynolds number (dimensionless), Sc = Schmidt number (dimensionless), D (cm^2s^{-1}) is the diffusion coefficient of the metal vapour in air, W (cm) is the width/diameter of incinerator, C (gcm^{-3}) is the saturation concentration of the *pure* metal $M_{th,i}$ (gs^{-1}) is the ideal entrainment rate of metal i in the gas and f (dimensionless) is an empirical constant accounting for binding of the metal to the waste matrix. F is calculated by taking the ratio of the measured mass flow rate $M_{m,\,i}$ (gs^{-1}) over the theoretically calculated rate $M_{th,\,i}$ (gs^{-1}).

$$f_i = \frac{M_{m,i}}{M_{th,i}} \quad (9)$$

Collection efficiency of the fabric filter is calculated using a stage efficiency for each particle size range:

$$n_j = 1 - \exp\left(\frac{-4aE_{\sum j}t}{\pi d_f}\right) \quad (10)$$

where n_j (dimensionless) is the stage efficiency, α (dimensionless) is the solidity of the fibres, E i(dimensionless) s the fibre capture efficiency, t (cm) is the filter thickness, d (cm) is the fibre diameter.

E is the total collection efficiency, determined by a number of different collection efficiencies, based on different collection methods:

$$E_{\sum j} = E_{R,j} + E_{I,j} + E_{D,j} + E_{DR,j} \quad (11)$$

Where the separate components are for interception, impaction, diffusion and interception-diffusion respectively (each dimensionless).

The total APC device efficiency for a metal i can is calculated using:

$$n_i = \frac{\sum n_j . \Delta m_{j,i}}{m_i} \quad (12)$$

where $\Delta m_{j,i}$ (g) is the fraction mass of metal i of particle size d_{pj}, and m_i (g) is the total mass of metal i.

Thus if the efficiency of the bags is known, along with the mass flow rate into the filters, then the emission of metallic aerosol not collected, $M_{out,i}$, (g) is:

$$M_{out,i} = M_i(1 - n_i) \quad (13)$$

The thermodynamic model is relatively advanced for its time, considering 6 metals (As, Cd, Cr, Hg, Pb, Sn), with a variety of oxide and chloride compounds for each. However, metal-metal interaction, including slagging reactions, are largely ignored. An empirical correction factor is used to account for non-ideality, such as a lack of equilibrium. This factor is again calculated using the ratio of the observed and calculated transfer coefficients to the raw flue gas. Although such empirical factors may not seem an ideal solution to a modelling problem, the result is a model which does at least provide realistic predictions of metal behaviour (Wu and Biswas, 1993).

Summary

Knowledge of aerosol systems is very good, and thus the modelling can be accurate and informative. Many groups have invested considerable time and effort in the development of the understanding of aerosol dynamics in combustion systems. The limitations are knowing how much metal is present in the vapour phase, and is thus available to condense, and whether this condensation is solely passive, or if it is reactive (i.e. "sticky" melts). Most of the work focuses on fuels which are better characterised than is MSW.

It is therefore once again apparent that good fundamental data and thermodynamic predictions will precede the further useful development of this strategy in connection with metal behaviour in MSWI. The best aerosol dynamic techniques often rely on the input of other modelling strategies, such as thermodynamics, to provide data for the aerosol dynamic modelling stages, so cannot be used in isolation. Indeed, without a good basis of thermodynamic data, the aerosol dynamic models can become highly empirical, and so loose their value in rationalising observed measurements with fundamental scientific principles.

2.6.4 Full Kinetic Modelling

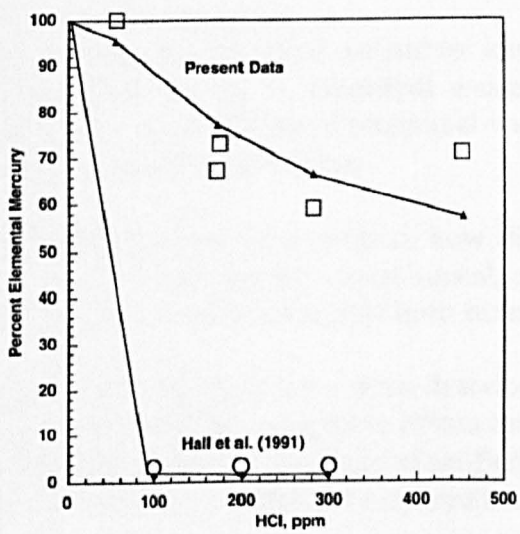
It has been explained that the assumption of equilibrium may not be reasonable for a "real" combustion system, but the problem has not really been addressed. Computationally, obtaining an equilibrium or aerosol dynamic solution can be extremely complex, and the added aspect of a kinetic correction would make it even more so. Although empirical kinetics are understood to a certain degree, a full kinetic explanation for all the reactions required, at furnace temperatures, is a long way from realisation, and remains a significant challenge.

An interesting recent development is in computational methods of inferring reaction kinetics through Gaussian modelling of molecular geometry. Rather than calculate reaction kinetics from experiment, which can be very complex, and require specialist equipment for very fast reactions, reaction kinetics can be calculated from information on molecular geometry and reactivity.

One paper looked at homogeneous reactions between metals and chlorine or oxygen (Hranisavljevic and Fontijn, 1997). In this case, a homogeneous reaction is one in which both reactants are in the same phase. The paper shows, both computationally and experimentally, that Cd in its ground state does not react with O_2 or HCl, but will react with Cl_2. The authors infer that Zn will behave the same, and that Hg will not react appreciably with either Cl_2 or O_2 in a homogenous fashion. The paper "proves" a potential homogenous route for $CdCl_2$ and $ZnCl_2$ production, but doesn't consider heterogeneous routes. In that the work finds no homogeneous routes for mercury, so only heterogeneous routes would be available, it demonstrates that both homogenous and heterogeneous routes must be considered for a complete model of metal behavior in incineration.

Using similar techniques a kinetic model was produced, supported by good experimental evidence, for oxidation of mercury by chlorine species (Sliger et al., 2000). It was an impressive attempt to incorporate computational prediction of the kinetics of reactions (based on molecular geometry and transition state energies) into a more conventional thermodynamic prediction of likely reaction routes. As it deals with mercury, all products are gas-phase at the temperatures considered, so the additional complexities of aerosol dynamics can be ignored. It can be seen in Figure 11 that agreement between experimental data (squares) and the model (solid black line) is very good. Although the work is very interesting, it is not envisaged that such methods could be included in a more general model for multiple metals, except at the most empirical level, due to the ever-increasing complexity of the modelled problem.

Figure 11: Kinetic modelling of the oxidation of mercury



The computational prediction of kinetics is most interesting, and offers great potential for further work in the future. The use of reaction geometry and molecular symmetry is becoming routine in the understanding of reactions of simple molecules, and as computation becomes faster, and the technique more universally applicable at a range

of temperatures, it may be anticipated that it could provide extremely useful information on combustion reactions.

However, despite the very interesting results from this type of modeling, it is evident that the technique is as yet insufficiently developed to be able to provide kinetic predictions for the whole of a combustion system at the present time. The work presented in these two papers, which must represent many months of work, considers just some of the possible reaction routes of a handful or reactants. Many more reactions would have to be considered to describe the whole combustion process. As more work is done in the area kinetics may well become a very powerful tool capable of providing further useful information on which to base "total" models of the behavior of metals in incinerators. If computational methods and computing power continue to increase as they have done in recent years, it may be anticipated that such techniques will grow in their application to combustion in the near future, as have thermodynamic techniques in the recent past. Recent developments already indicate that this is a powerful technique which has the potential to contribute a great deal to the understanding of reactions in combustion systems (Backreedy et al., 2003).

2.6.5 Overview of Modelling Techniques for Metals in MSW Incinerators

It has been shown that thermodynamic, aerosol dynamic, kinetic, and combined model predictions can be powerful tool in predicting and explaining the behaviour of reactions occurring in thermal systems at high temperatures. It has also been seen that further development of such models to describe municipal waste incineration would be beneficial, as computational limitations experienced in earlier models are being overcome with faster hardware and more sophisticated software. Furthermore, it has been shown that such thermodynamic data can provide a source of input data for aerosol dynamic modelling of incineration processes, which can better describe the overall behaviour of vapours and particles in an incineration system. It is clear that computer modelling may help to explain and predict metal partitioning in waste combustion systems working under different operating conditions.

2.7 Chapter Summary

This chapter has reviewed the current knowledge, as presented in the literature, on the behaviour of metals in municipal waste incineration. Background information has been given on the nature of municipal waste, and its arising, and of pollution concerns caused by waste incineration.

Detailed study has been made of how metals partition in waste combustors, and why this is of environmental, toxicological, and environmental concern. The sources of these metals in waste have also been examined.

Analytical techniques have been described which allow for the analysis of metals in incinerator residues, in order to obtain further information on metal partitioning during combustion. A need has been identified for improved techniques of continuous flue gas monitoring, to obtain new information on the combustion process.

Finally, it has been shown how computer modelling techniques can increase understanding of the behaviour of metals in incinerators. However, the nature of these models can become extremely complex, and both data and computational requirements may be high.

While the information available on the combustion conditions and waste input remains as it is, it would seem futile to attempt to develop such a complex model for such a variable combustion process. It is therefore thought better to concentrate efforts on obtaining new fundamental experimental data on the incineration process, particularly with respect to temporal variations, rather than to produce highly sophisticated models without adequate practical verification. Nevertheless, thermodynamic and other modelling could be extremely useful for analysing and explaining the data obtained, and for sensitivity analyses, to see which factors are most important in determining metal partitioning, and hence causing temporal fluctuations. The use of smaller-scale laboratory combustion experiments, using a test furnace, may help to prove suggested links between observed and modelled predictions of metal behaviour.

The remainder of this thesis describes new advances made in analytical methods for investigating temporal variations in waste combustion systems, which have substantially increased the knowledge on how these systems operate. Using the data obtained from these experiments, thermodynamic models have been used to link these temporal variations to changes in both waste feed and incinerator conditions. A series of calculations have formed a sensitivity analysis for the effect of different variables on the combustion system, and have also considered the effect of inhomogeneity of the waste feed.

Chapter Three:

Experimental Programme

Having identified that further information was required on the release of metals during waste combustion, particularly with respect to temporal variation in signals, a unique continuous monitoring system was designed, built and tested for the purpose. Collaboration between the University of Sheffield and SPECTRO Analytical Instruments GmbH & Co Kg led to the production of a unique, movable laboratory, capable of the continuous monitoring of elemental pollutants in gaseous samples, and based upon ICP-OES technology.

The development of this Continuous Emissions Monitoring Laboratory (CEML) allowed the real time investigation of elemental pollutant emissions in the gaseous and particulate phases. This system provided sensitive and simultaneous multi-element detection of entrained metal aerosols and vapours by direct injection of a stream of sample gas into the spectrometer, using a specially modified plasma torch. Direct analysis of metals in the sample stream eliminated the need for time consuming, labour intensive and often un-reliable conventional solids analysis procedures, and enabled continuous monitoring of process emissions.

This chapter describes the analytical facility in detail, describing its optimisation and testing; including preliminary laboratory furnace experiments, and goes on to describe a detailed investigation into metal behaviour at a full-scale commercial incineration plant, using this unique instrument.

3.1 Description of the Continuous Emissions Monitoring Laboratory

3.1.1 External Appearance

The CEML is a self-contained mini laboratory that is transportable using a crane and lorry. The CEML was designed and built by project collaborator Spectro AI, (Kleve, Germany). The dimensions of the CEML are 6.5m x 2.4m with an overall height of 3.5m, and a nominal weight of 7.2 Tonnes. The laboratory is shown in Figure 12. The laboratory requires a mains power supply of 30-40 kVA, which is supplied through an externally mounted 40kVA transformer, to allow for variations between on-site power supplies. The configuration generally used is for a 3-phase, 415V, 63A supply. Other than this, the only external requirements for this self-contained laboratory are mains water, and liquid argon deliveries about every 5 days during continuous operation.

Figure 12: Photograph of CEML system during transport from Buxton research site.

3.1.2 Schematic Overview of Laboratory Design

The internal design of the laboratory is based around the requirements for successful continuous monitoring of flue gases. These are: the continuous isokinetic withdrawal of a sample from the process being monitored, a secondary isokinetic sub-sampling stage (to reduce the sample volume to that required for analysis), a detection system, which can be calibrated for flue gas analysis, and a means of recording the data obtained. These schematic components are summarised in Figure 13.

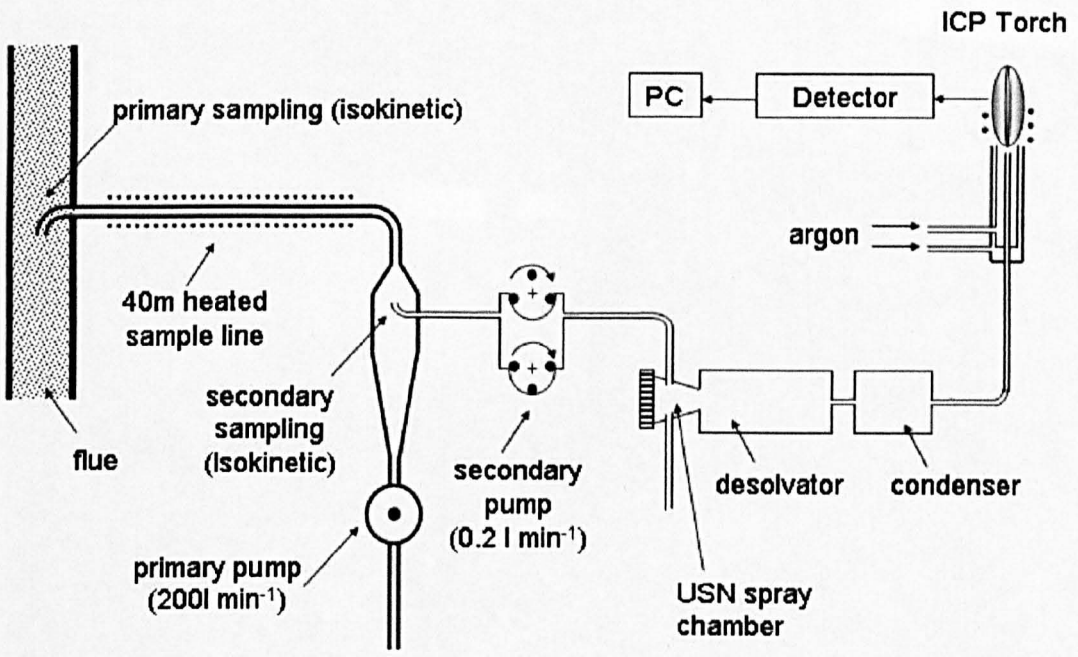


Figure 13: Schematic diagram showing CEML configuration

In addition to these essential components, the laboratory is required to provide a robust, clean, temperature-controlled environment in which successful analytical measurements could be made at industrial locations, with little external support. To facilitate this, the cabin is fully air-conditioned, and was equipped with normal "wet chemistry" facilities, storage space, personal protective equipment (PPE), and a range of spares in order that the system can be repaired or adapted as required during on-site work. The options available also mean that the instrument can easily be re-configured for conventional analysis of liquid samples.

3.1.3 Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES).

The main instrumentation in the CEML is a Spectro Ciros-CCD ICP-OES (Figure 14) with radial view configuration (SPECTRO Analytical Instruments, Kleve, Germany). Unlike axially viewed plasma systems, the radial plasma optics are especially suited for field analysis as no optical interface cooling is required, which is advantageous as cooling systems can be unreliable. The torch used for flue gas analysis was a custom built demountable torch, designed to allow for the higher flow of coolant gas and higher power needed to sustain the plasma whilst using atmospheric and flue gases as the sample matrix. Calibration was via an ultrasonic nebuliser, which provided a dry aerosol of metals to the ICP, and also normalised the water content of gas samples introduced to the system.

Figure 14: SPECTRO CIROS ICP-OES system used in the CEML

The detection system used with the inductively coupled plasma is optical emission spectroscopy (OES). The "CIROS" name of the ICP-OES stands for CIRcular Optical System. The CIROS detectors do not require on-chip cooling and produce the fastest throughput of any solid-state detector ICP. When atomic species reach the plasma, the energy applied causes excitation, or ionisation, and characteristic emission of radiation occurs as elements return to lower energy levels (relaxation). The radiation emitted is of specific wavelength, thus allowing un-ambiguous identification of different elements. Emitted light is passed to the spectrometer optics via an optical fibre, where metal emissions are measured by means of a CCD array. The radiation intensity, which is proportional to the concentration of the element in the analyte, is recalculated internally from a stored set of calibration curves and can be shown directly as percent or measured concentration. The CCD detector is capable of measurement of a large number of wavelengths at the same time, and thus simultaneous quantitative detection is possible for a large number of elements using this detection system. A wide range of wavelengths may be measured (125 nm - 770 nm), which means that there are usually several good (interference free) emission lines available for most metals, meaning that accurate quantification is possible. Many of these emission lines are not available on older instruments, due to less sophisticated optical and detection systems. The detectors in the CIROS have a pixel resolution of 9 picometers (0.009nm), and are well suited for difficult matrices like flue gas, as high resolution reduces interferences from overlapping emission lines.

Analytical Plasma

The plasma torch consists of three concentric quartz tubes, with the inner tube containing the sample gas aerosol and Argon support gas, and the outer tubes containing an Argon gas flow to cool the tubes and shape the plasma, and is based on

the design by Trassy (Trassey, 2001). A radio frequency (RF) generator (1000-1700 W, 27 MHz) produces an oscillating current in an induction coil situated around the tubes. The induction coil creates an oscillating electric field, which produces an oscillating magnetic field. The magnetic field in turn sets up an oscillating current in the ions and electrons of the support gas. These ions and electrons transfer energy to other atoms in the support gas by collisions to create a high temperature plasma, as shown in Figure 15. The torch is demountable, with interchangeable quartz tubes,. For gas phase analysis the diameters of the tubes are larger than in torches used in aqueous analysis, and the RF power used is generally higher (1600-1700w). The basic reason for these differences is that gas samples have large concentrations of molecular gases (N_2, CO_2, O_2), and excitation of such molecular species absorb large amounts of energy from the plasma. Thus high RF power is used to ensure adequate excitation of analyte species, and this in turn requires higher argon flows and a larger torch, in order that the plasma shape, and stability is maintained.

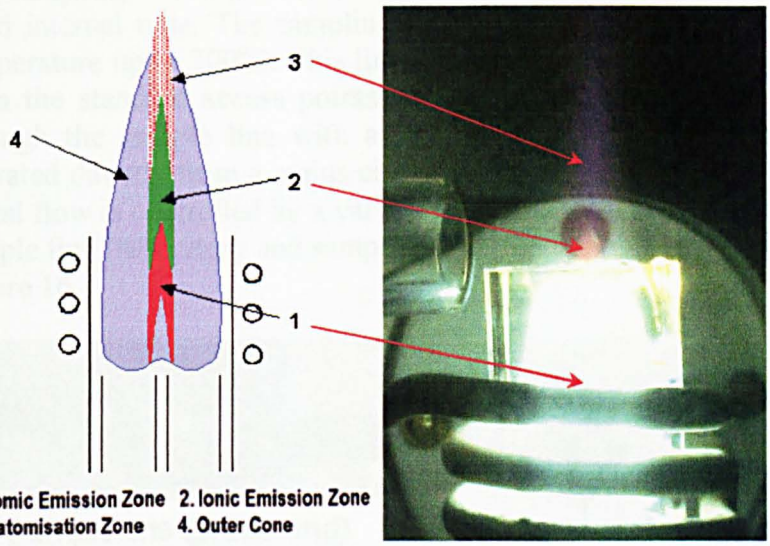


Figure 15: Schematic diagram of a plasma (left), photograph of plasma (right)

In operation, the sample aerosol is instantaneously decomposed in the plasma (plasma temperature is in the order of 6000 - 10000 K) to form analyte atoms and ions. As they loose energy through a process known as relaxation, the ions and excited atoms emit light of a characteristic wavelength depending on the electronic transitions occurring. Figure 15 shows a schematic diagram of the structure of the plasma. There are three distinct zones that are of interest. Lowest is the atomic emission zone or induction zone, where the energy from the RF coil is focussed. This area has a lower excitation temperature than higher in the plasma and emissions here are primarily atomic. The temperature of the plasma increases and reaches a maximum towards the middle, in the ionic emission zone. It is in this zone that the best analytical measurements will usually be made. It is possible to optimise the analysis by adjusting the torch height so that the spectrometer window is in line with the optimum region for the elements being determined, although for multi-element determination, a compromise position must be chosen. Above the ionic emission zone, the plasma temperature falls, as energy is dissipated away from the plasma. Ions and electrons re-combine to form atoms, and further light is emitted as further relaxation occurs in the region known as the re-atomisation zone. Surrounding all three of these zones is the

outer zone, which is primarily comprised of argon gas, which isolates and helps to maintain the plasma.

3.1.4 Laboratory Equipment, Services and Facilities

Sample Collection System

The laboratory is equipped with a specially designed sample collection system, to ensure that the sample reaching the ICP is representative of the bulk gas being measured, and does not degrade, or deposit, before reaching the plasma. A primary sample is taken isokinetically from the gas being measured, at a relatively high flow rate. This is then sub-sampled for introduction into the ICP. A sophisticated calibration system ensures that quantification is accurate and precise.

Primary Sample Collection

The sampling line that is used in the CEML is a 40m-heated line with a 12mm PTFE lined internal tube. The sampling line, heated in three segments, can be operated at temperature up to 200°C. This line allows for collection of representative gas samples from the standard access points on most industrial plants. The sample is pumped through the sample line with a high flow rate heated membrane pump, which is operated directly from a mains circuit. Operating at a nominal flow of 120L min^{-1}, the actual flow is controlled by a valve, with the flow being measured by a rotameter. The sample line (laboratory and sampling ends, including sample probe in-situ) is shown in Figure 16.

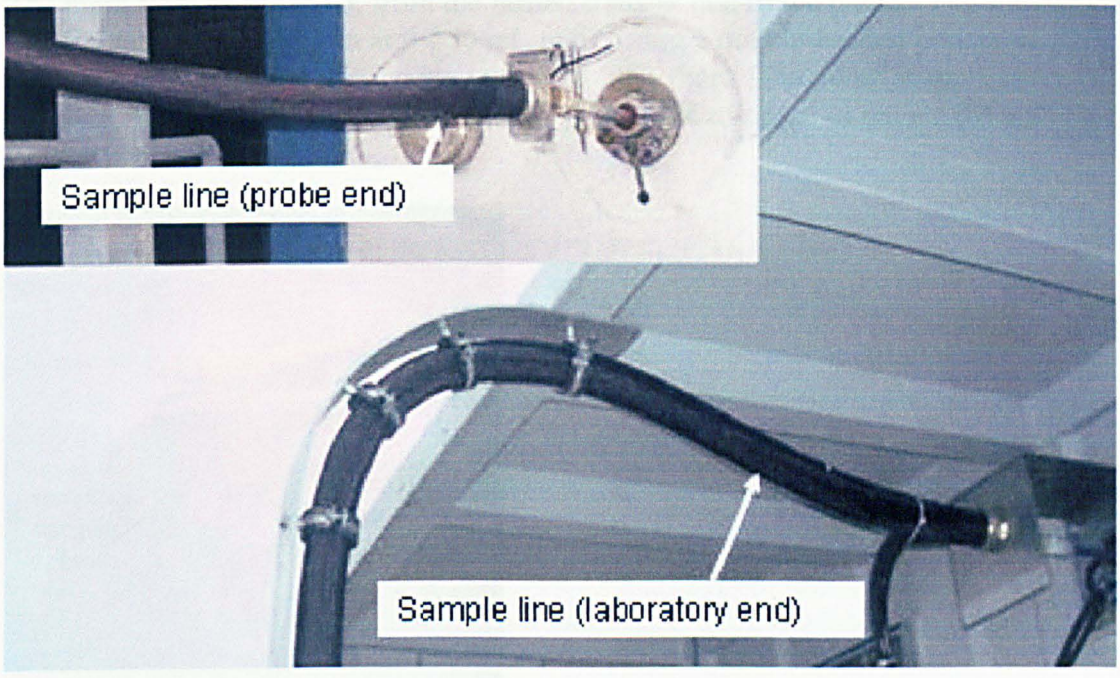


Figure 16 - Photograph of heated sampling line at laboratory and sampling end (inset)

The probe used was an adapted BCURA probe (Figure 17); which had a series of interchangeable tips of different diameter, allowing isokinetic sampling from gases with a range of velocities.

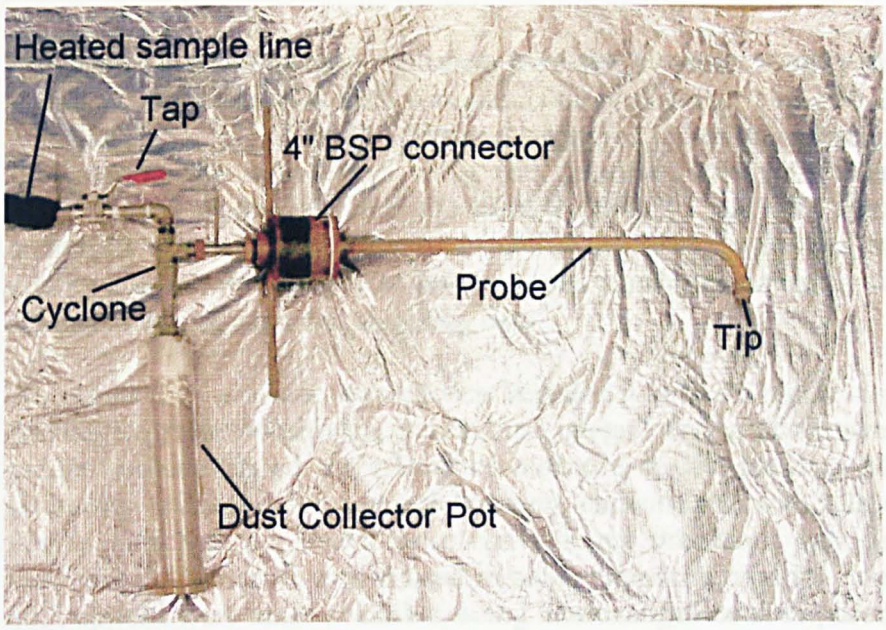


Figure 17: The adapted BCURA sampling train

Secondary Sampling Head

The secondary sampling head has been developed to allow the sub-sampling of the main flue gas sample at a flow rate that can be introduced into the plasma (Figure 18). Simply, it is a second isokinetic sampling stage, based around smaller mass flows. The main flow of gas is up, from the heated transfer line to the pump. The sub-sample is collected by the side arm at 0-260 mL min^{-1} using a double-headed peristaltic pump. The tubing used is Tygon Silicone with a i.d. of 1.6mm. The pump is the Master Flex supplied by Cole-Palmer. The pump heads are set out of phase to reduce the pulsing of the sample.

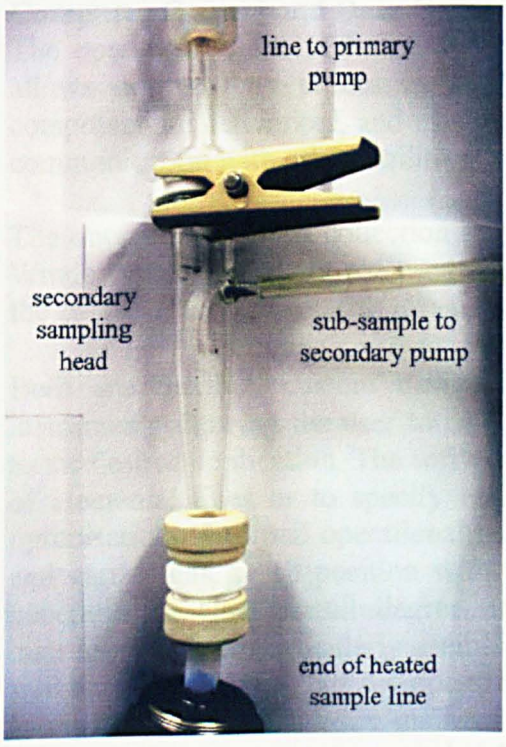


Figure 18: The sub-sampling system at the laboratory end of the transfer line.

Nebuliser
Calibration standards are aspirated into the plasma, usually using an ultrasonic nebuliser in conjunction with a cyclonic spray chamber (Spectro USN200 Ultrasonic Nebuliser). Sample gas with additional argon is used as the nebuliser gas. The addition of water to the sample gas using the nebuliser, and subsequent desolvation and condensation normalizes the moisture content of the gas stream, thus reducing analytical error. Also the ability to add standards into the gas stream is useful for quality control, through the addition internal standards, and periodic calibration check standards during extended sampling runs.

An ultrasonic nebuliser was chosen because it offered higher aspiration efficiency, leading to greater sensitivity, and because integral drying of the sample with heater and peltier cooler reduced the effects of moisture on the plasma. However, long-term reliability and consistency problems were encountered with this complex electronic device, which meant that a more conventional pneumatic nebulising system with a modified lichte nebuliser was used in some situations, and for liquids analysis. Thus both options were made available, being interchangeable as required.

For calibration purposes, the gas matrix used must closely match that encountered in the flue gas being measured. When the gas composition in the flue gas was consistent, and could be obtained "clean" (i.e. without significant metal concentrations), the flue gas itself was used as a calibration matrix. Alternatively, a synthetic "flue-gas like" matrix could be synthesised from the calibration gas cylinders (oxygen, carbon dioxide, nitrogen), which are described below. Matching of the calibration gas matrix to the sample composition ensures an accurate calibration, essential for reliable quantification. Where the analyte matrix varied significantly with time (e.g. variable carbon dioxide content of the flue gas), a series of calibrations were performed, and the ICP signal was correlated both to analyte concentration and matrix composition.

Computer Control and Data Collection System
The operation of the ICP-OES is via computer control. A second PC and printer allows on-line data processing simultaneously with data collection. These two computers are networked, and may also be connected to an external network, to allow communication with other facilities.

The operation and data collection system used to control the ICP-OES operates under Windows 2000. Initially, the programme used was Spectro Smart Analyser, but during the course of the project, this was upgraded to the Spectro Vision platform.

Both are flexible, custom designed control software packages for the Spectro instrument, allowing the user to develop analytical methodologies that are applicable to the desired application. The software allows the users to choose from either a library of elemental lines or to specify emission lines of choice. The system also allows optimisation of normal operational parameters, such as flow rates for sample, coolant and carrier gas, torch position with respect to detector, and RF energy for plasma generation. This overall degree of control is rarely seen in modern analytical instruments and is particularly useful in a research environment such as this, where the sample matrixes, and thus the operating parameters, are often highly un-conventional. In terms of this project, the main advantages of the new "vision" software over the older programme are an improved stability, general layout and simplicity of operation, and the ability to save the entire measured spectrum for each result, allowing re-

calculation of results, and examination of different regions of the spectrum at a later date, if it is subsequently discovered after measurement that omissions have been made in the method used.

Power
Power requirements for the CEML are relatively high, due to the power consumption of the ICP itself, the heated sample lines, and air conditioning, as well as general equipment in the laboratory.

Internally, electrical power is distributed throughout the CEML from a switching panel, which provides 3-phase, 415V to the ICP-OES and a single phase, 240V supply on various circuits throughout the lab. All the major systems are on individual circuit breakers, and where appropriate residual current devices. This allows for both ease of operation and increased safety. All power outlets within the CEML meet the required standards, and are of European socket design, reflecting the origin of the equipment. The CEML also has battery powered emergency lighting, which operates in the event of power failure.

Argon Supply
Argon used by the ICP-OES is supplied from either four-200bar gas cylinders or from a liquid argon tank. The preferred alternative is the use of liquid argon, which is supplied from an externally mounted 230L capacity Cryotank. The liquid argon Cryotank meets the latest EU safety standards and can be transported whilst loaded. Liquid argon is both cheaper and provides higher purity argon gas than do the cylinders. The Cryotank is filled as required from a road tanker, either directly to the tank if access allows, or through a fill point at the far end of the CEML. A 230L tank of liquid argon will supply the CEML with argon gas for approximately one month of normal operation, or 5 days of 24-hour continuous monitoring, having only a minimal (~2%) bleed off. Alternatively, the CEML may be run from argon gas cylinders operating on an automatic change-over system. However, the rate of gas consumption is approximately 2 x 200bar cylinders for every 10 hours of operation, making this an expensive way to operate the CEML.

Calibration Gases
The calibration gases are used to prepare artificial gas mixtures that mimic the gas compositions found in the flue gases, as is required for accurate system calibration. Oxygen, nitrogen and carbon dioxide were used. The gas cylinders are externally mounted, and gases are piped to a set of rotameters inside the cabin, which were used to set the desired gas mixture being fed into the analytical system.

Climate Control
To ensure optimum performance from the ICP-OES, the CEML has full climate control using a heating-cooling air conditioning system, as the operation of the instrument is temperature-sensitive. This well specified 10kW system provides both temperature control, and cleans the air in the laboratory, even in extremes of ambient temperature as may be found near operational units during on-site measurement.

Water Supply
The CEML can be connected to the mains water supply through an extension hose. There is a sink, which drains externally. The CEML also has an on-line deionised water system, which connects to the main water supply. The deionised water is

supplied through a separate tap at the sink. There is also a conductivity meter that is used to measure the efficiency of the ion exchange cartridge.

General Fittings and General Laboratory Equipment
The CEML is supplied with one 150cm x 45cm workbench, one 200cm x 45cm computer desk, and one 150cm x 45cm computer desk. The CEML also has three storage cupboards and an automation cabinet. The automation cabinet was used to house gas analysers for CO, CO_2 and O_2 during some of the on-site testing. There is a 4-figure balance in the lab, allowing for accurate measurement of solid samples and, if necessary, standards.

The laboratory is a self-contained unit, and must provide all equipment for a sustained programme of measurements. Thus the unit is equipped with all the general glassware and equipment generally required in an analytical laboratory, including volumetric glassware, sample tubes, pipettes, measuring cylinders, beakers etc. The lab also has space to accommodate a reasonable quantity of spares and disposables, such as replacement peristaltic tubes, disposable sample containers, standards and reagents.

It should be apparent from the description above that the laboratory has been designed with a high degree of adaptability, as well as being equipped with a state of the art analytical instrument. The CEML is generously specified, and is capable of providing for the varied needs for analytical work in the harshest industrial environment. Thus the laboratory may be taken on-site for a programme of continuous monitoring, and is able to be adapted and optimised on site by an experienced operator, to allow successful measurements to be made, in a range of challenging analytical situations. Nevertheless, the nature of continuous monitoring requirements are such that the laboratory may operate continuously for many days at a time, with minimal supervision, meaning that reliability, robustness and safety have been paramount in the design of the unit,. With careful planning, the laboratory is quite capable of running for a week, 24 hours a day, with just occasional checks to ensure that everything is operating as it should be.

3.2 Development and Optimisation of the Continuous Emissions Monitoring Laboratory

3.2.1 Initial Investigation of Normal Operating Parameters

Standards and Calibration
Elemental calibration standards were prepared from a 20 ppm stock multi-element standard solution (Bernd Kraft GmbH Salze & Lösungen, Duisburg, Germany) covering the range 0.01 – 20 ppm. Standards used were 0.01, 0.1, 0.5, 1.0. 5.0, 10.0 and 20.0 ppm in each metal. These were introduced via the USN, which was also supplied with sample gas from the peristaltic pump (0-260 L min^{-1}), and nebuliser Argon (0.8 l min^{-1}). Normal ultrasonic nebuliser conditions are shown in Table 18, and are those recommended by the equipment manufacturer. Previous work on the transport properties of the USN (mass-flow calculations), showed that when nebulised, the standard solutions used corresponded to aerosol concentrations of 1.1 ng m^{-3} to 2.2 mg m^{-3}. Details of this calculation, which was periodically repeated (notably after repair/alteration to the USN system), are given in Appendix 3.

Table 18 USN operating conditions

parameter	value
heater temperature	150 -160 °C
cooler temperature	0 - 2°C
carrier gas flow	0- 0.32 L min^{-1}.

Line Selection, Plasma and Torch Optimisation, and Calibration in Flue Gases

Initial experimentation with the CEML quickly confirmed expectations that ICP operating conditions, and gas sample composition had a significant effect on signal quantification for metals being measured. A programme of experimental optimisation of the system for the analysis of metals in flue gases was undertaken, the key aspects of which are detailed below.

Line Selection and Background Correction

Most elements have a series of characteristic emission wavelengths which may be used to quantify metal concentrations. Initially, the most sensitive line was selected for each element, as recommended by the instruments generalised "optimal line" list, or by the recommendation of expert staff at CAS (Centre for Analytical Sciences, University of Sheffield). A list of some of these initial lines is given in Table 19. The background correction is a second measurement, taken just to the side of the emission line. This value is subtracted from the measurement of the intensity at the emission line, and effectively "zero's" the measurement each time, accounting for spectral shifts which may occur due to matrix changes. However, both the emission line and the background may suffer interference (from other emissions which overlap with the intended one). Thus the line selection and background corrections must be carefully chosen for successful quantification. Background correction was particularly important in this work, due to the flue gas matrix, which was more variable than a typical liquid matrix, and so tended to lead to greater spectral shifts, which would otherwise affect signal quantification.

Table 19: Generally suitable emission lines used initially for ICP detection, from liquid analysis

element	wavelength (nm)
carbon	247.856
nitrogen	174.273
oxygen	130.485
aluminium	167.078
antimony	206.833
arsenic	189.042
cadmium	214.438
chromium	283.563
cobalt	238.892
copper	324.754
iron	259.94
lead	261.418
manganese	257.61
nickel	341.476
sodium	589.592
thallium	190.864
tin	242.949
vanadium	309.311

Initially, air, and "synthetic flue gas", made up from the calibration gases supplied with the laboratory were used as a matrix in which to introduce standard solutions to produce calibration curves, to verify whether quantification could be achieved on the suggested emission lines. It was immediately seen that carbon dioxide level had a significant effect on some analytical line signals. The effects were variable, and included increasing or decreasing the gradient of the calibration line (i.e. sensitivity), or changing the intercept (i.e. signal zero noise). Some lines were rendered completely inappropriate, due to emissions from molecular gases over the region in which the emission line was situated, while others required careful use in the unusual matrix of a gaseous sample. Illustrative results are shown in Figure 19 - Figure 22.

Figure 19 illustrates the importance of the selection of an appropriate emission line for quantification, and also of a suitable background correction. It shows the measured emission signal in counts per second (cps) for cadmium, arsenic, and nickel. Although the cadmium emission line at 226.502nm has good sensitivity, it is not an ideal quantitative line without further confirmation (via a second monitored line), as it may suffer from a slight interference from As (0.04%, if analyte and interference are present at the same concentration). In addition, careful background is required, as background correction in the region of 226.45nm would tend to suffer from interferences from nickel.

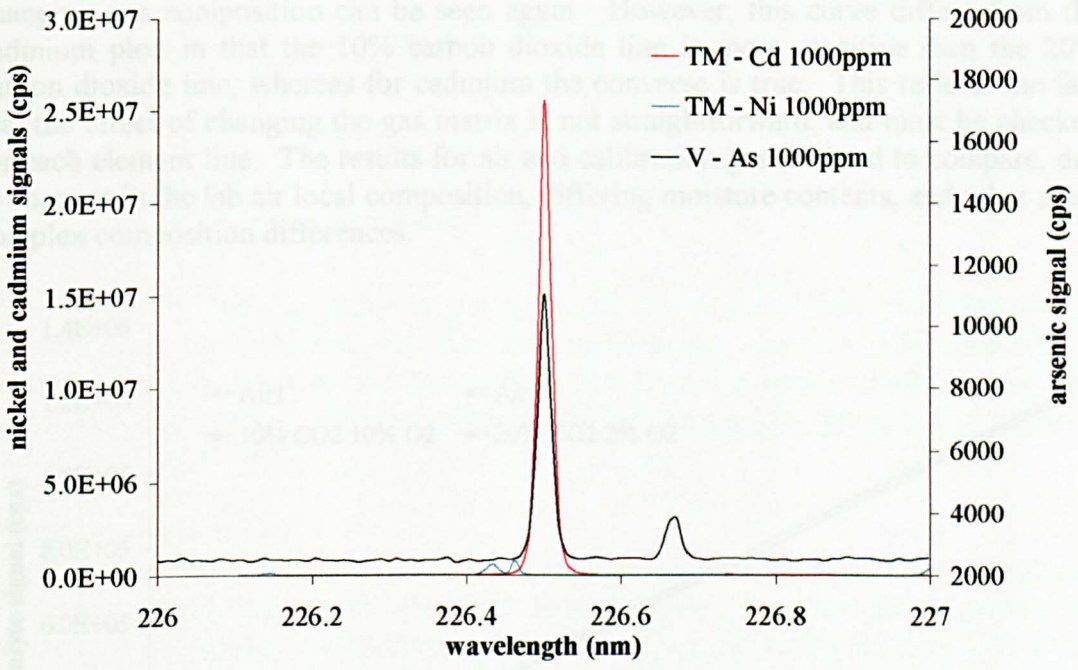


Figure 19: Emission spectrum in the region of the Cd II 226.502 nm wavelength

Figure 20 shows the calibration curve for cadmium, as measured on the more reliable 214.238nm wavelength. It can be seen that carbon dioxide concentration affects line sensitivity. Additionally, the y-axis intercept value changes, indicating that the gas matrix not only affects sensitivity, but background noise. However, the sensitivity of the line is much lower, leading to a count value of about half of that for the 226.502nm line, meaning that this wavelength is less good for the smallest signals. It is therefore useful to monitor both lines.

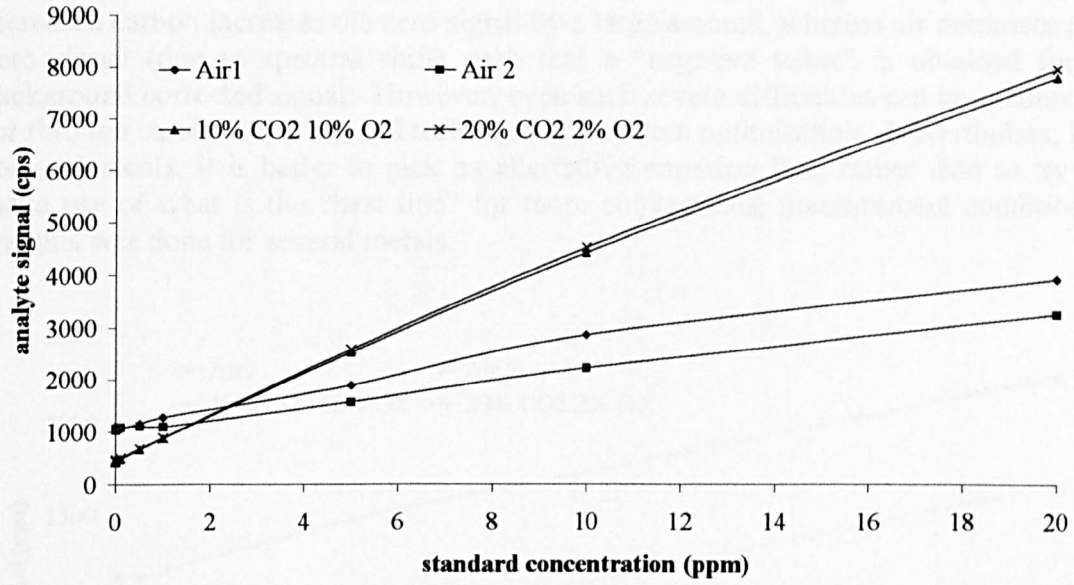


Figure 20: Calibration curve for cadmium on the Cd II 214.438 nm wavelength

Figure 21 shows the calibration curve for copper. The change in sensitivity with changing gas composition can be seen again. However, this curve differs from the cadmium plot, in that the 10% carbon dioxide line is more sensitive than the 20% carbon dioxide line, whereas for cadmium the converse is true. This reflects the fact that the effect of changing the gas matrix is not straightforward, and must be checked for each element line. The results for air and calibration gas are hard to compare, due to changes in the lab air local composition, differing moisture contents, and other more complex composition differences.

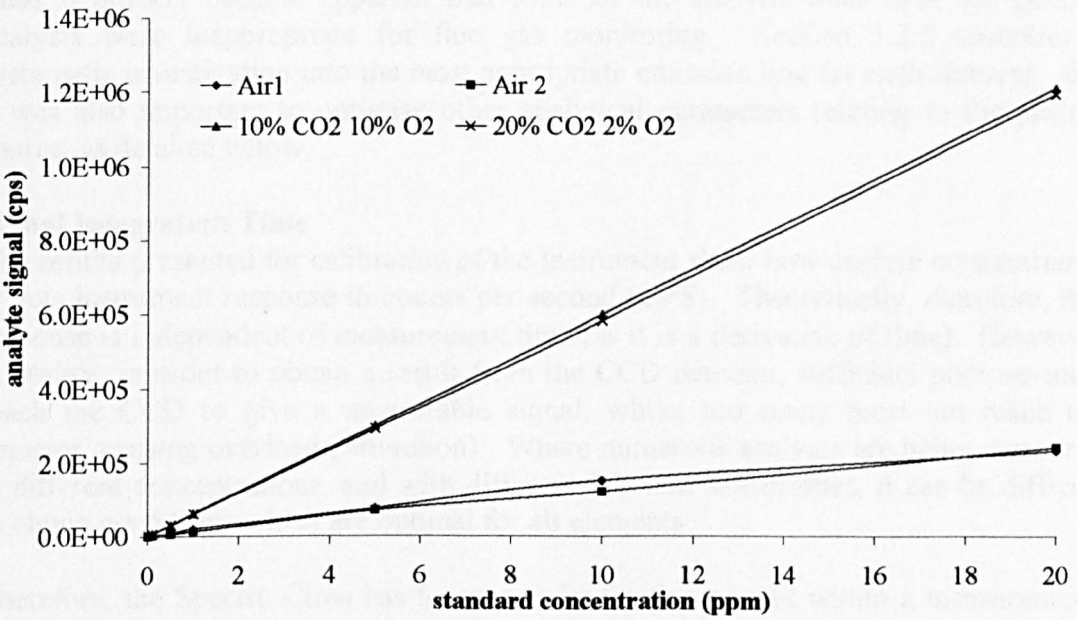


Figure 21: Calibration curve for copper

Figure 22 shows the calibration curve for thallium, which in many ways is a worst-case scenario. Poor sensitivity is indicated by a low count value, even for the highest

concentration standards. Line gradient (sensitivity) changes with gas composition, and increased carbon increases the zero signal by a large amount, whereas air decreases the zero signal (due to spectral shift) such that a "negative value" is obtained for a background corrected signal. However, even such severe difficulties can be accounted for through careful experimental technique and system optimisation. Nevertheless, for some elements, it is better to pick an alternative emission line, rather than to try to make use of what is the "best line" for more conventional measurement conditions, and this was done for several metals.

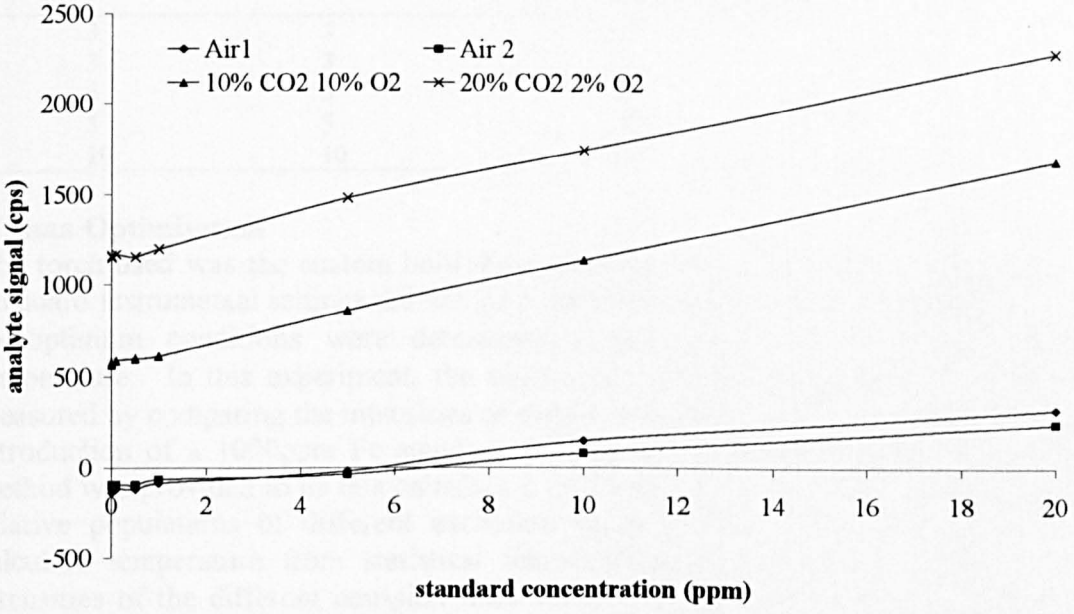


Figure 22: Calibration curve for thallium

Thus it quickly became apparent that some of the analytic lines used for general analysis were inappropriate for flue gas monitoring. Section 3.2.2 describes a systematic investigation into the most appropriate emission line for each element. But it was also important to optimise other analytical parameters relating to the plasma source, as detailed below.

Signal Integration Time

The results presented for calibration of the instrument show how analyte concentration affects instrument response in counts per second (CPS). Theoretically, therefore, this response is independent of measurement time (as it is a derivative of time). However, in reality, in order to obtain a result from the CCD detector, sufficient photons must reach the CCD to give a measurable signal, whilst too many must not reach the detector, causing overload (saturation). Where numerous analytes are being measured at different concentrations, and with different inherent sensitivities, it can be difficult to obtain conditions which are optimal for all elements.

Therefore, the Spectro Ciros has 5 separate integration phases within a measurement, of different durations. These operate sequentially, to allow different integration times for different elements. For most gas-phase monitoring, a very long integration time of 44 seconds was used, to obtain maximum sensitivity for trace elements (whilst also providing short integration phases within this time to measure bulk constituents). At other times, a shorter integration time of 24 was used, in order to obtain better

temporal resolution of changing signals. While the phase time is an important variable, it is difficult to simply demonstrate its effect, and the values chosen largely arose from advice from other users of the ICP system, and of our own experience. Typical integration times, and the associated phase times are shown in Table 20.

Table 20: Integration and phase times for OES detection

phase	24 second liquid measurement	24 second gas measurement	44 second measurement (clean flue gas measurements)	44 second measurement (un-clean flue gas measurements)
1	3	3	3	1
2	3	3	3	1
3	3	3	3	4
4	5	5	15	8
5	10	10	20	30

Plasma Optimisation

The torch used was the custom built demountable torch described in section 3.1.3 . Standard instrumental settings did not give optimal sensitivity with the modified torch, so optimum conditions were determined experimentally by measuring plasma temperature. In this experiment, the electronic temperature within the plasma was measured by comparing the intensities of sixteen iron emission lines resulting from the introduction of a 1000ppm Fe standard solution to the plasma via the USN. This method was provided to us in a calculation by Trassy (Trassey, 2001), based upon the relative populations of different excitation levels of iron, which can be used to calculate temperature from statistical thermodynamics theory. The ratio of the intensities of the different emission lines varies with temperature, as the Boltzmann distribution of energy levels of electrons in the iron change. For analytical purposes, a high temperature is desirable to ensure adequate excitation of all elements, but stability is also required, such that small fluctuations in measurement conditions (e.g. sample matrix) do not unduly affect signal quantification.

Using this method, plasma gas flows, i.e. injector flow (sample and nebuliser gas), auxiliary flow, coolant flow, and RF power were optimised. Sample gas flow is set on the external peristaltic pump (secondary sampling pump), while the rest of the variables are controlled by the operating software. The results of these experiments are given below.

Injector Flow

The gas through the torch injector was made up of two separate flows; the sample gas (from the flue) and the nebuliser "make up" gas (argon).

Sample Gas Flow Rate

The gas was sub-sampled from the primary pump using the secondary sampling head and a peristaltic pump. In order to achieve the lowest limits of detection it was necessary to have the largest sample flow rate that the plasma could sustain, as the more sample enters the plasma, the more may be excited to give analytic emissions. Figure 23 shows the sample gas flow rate against plasma temperature, and it can be seen that increasing sample flow rate decreases plasma temperature somewhat. This is due to the quenching effect of molecular gases in the sample matrix, which very effectively absorb energy from the plasma. Thus a balance must be made between increasing sensitivity by increasing sample throughput, and decreasing it by reducing

excitation temperature. A sample flow rate of 240 mL min^{-1} was chosen, as the negative effect of plasma cooling was small compared with the positive effect of increasing sample throughput. At higher flow rates, plasma stability became a problem, with the plasma being "blown out", and at lower flow rates, maintaining the sample "channel" through the plasma can be problematic, reflected by the increased variability (deviation from a smooth trend) at low flow rates.

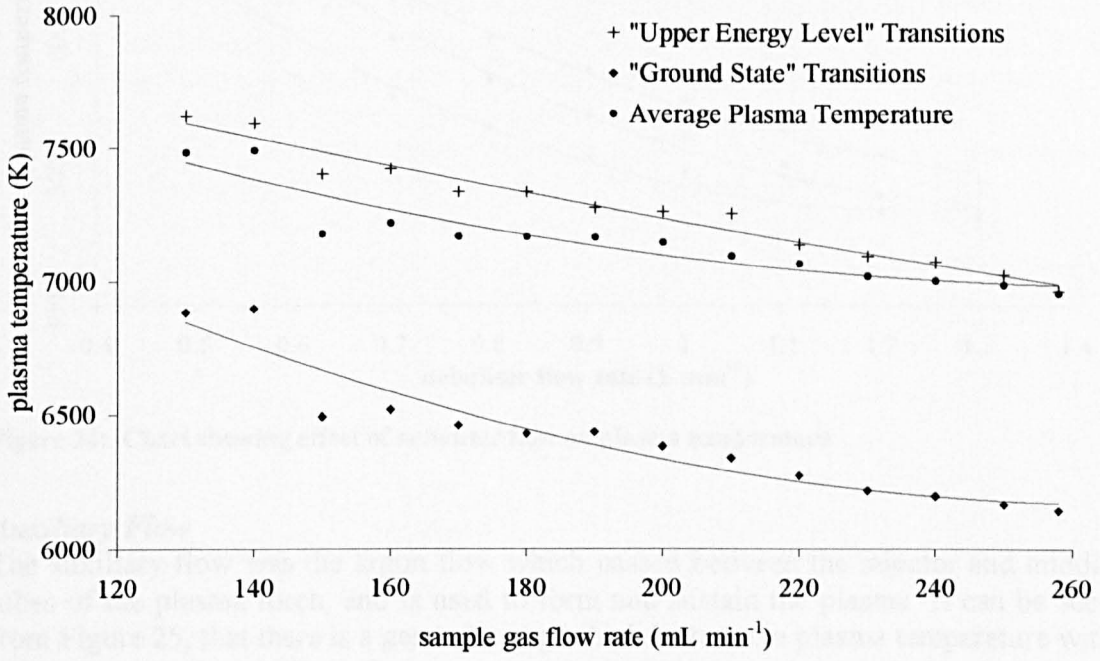


Figure 23: Chart showing effect of sample gas flow on plasma temperature

Nebuliser Flow

The nebuliser flow is an argon "make up" gas that provided extra argon (to help sustain the plasma), mixed with the sample gas, and to provide enough flow to break through the viscous surface of the underside of the plasma. The optimum nebuliser flow rate provides enough flow to achieve its purpose without reducing the temperature of the plasma to such a level as to lose sensitivity, or reducing the gas residence time in the plasma so much that the atoms/ions are not fully excited before leaving the plasma. Figure 24 shows effects of increasing nebuliser flow rate on plasma temperature. It can be seen that the effect of this variable is significant, with high flow rates having a detrimental effect, with the gas sample effectively being "diluted" with argon. A reasonably low value of 0.7-0.8 L min^{-1} was selected, but values below this were avoided, due to the occurrence of plasmas stability issues, when the sample gas was unable to effectively maintain a channel through the centre of the plasma.

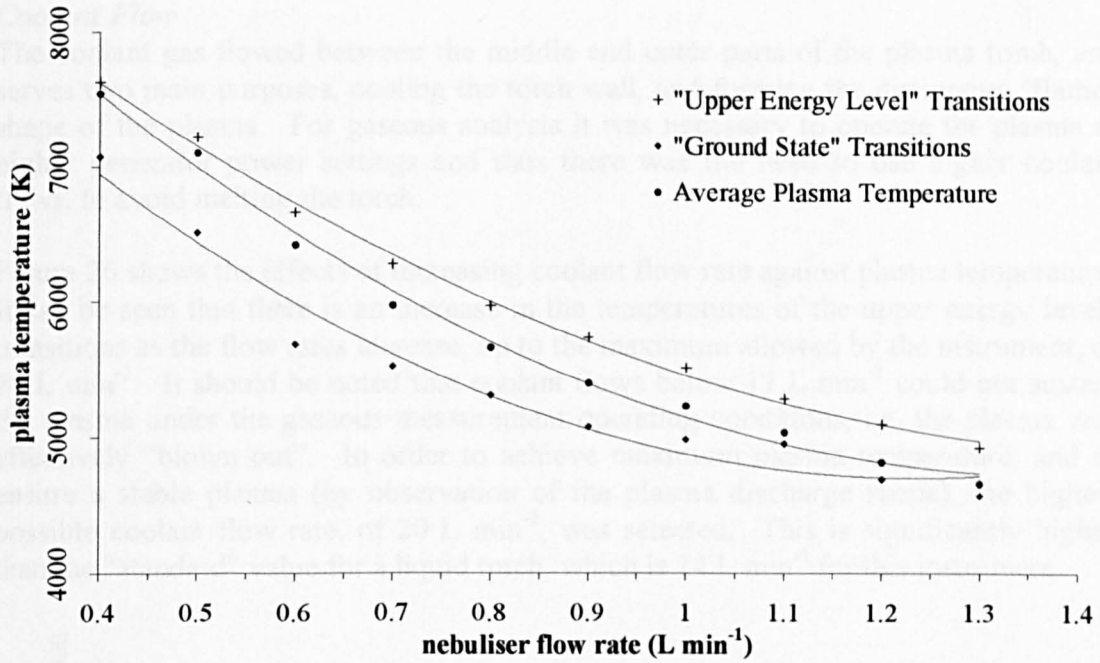


Figure 24: Chart showing effect of nebuliser flow on plasma temperature

Auxiliary Flow

The auxiliary flow was the argon flow which passed between the injector and middle tubes of the plasma torch, and is used to form and sustain the plasma. It can be seen from Figure 25, that there is a general and gradual decrease in plasma temperature with the increase in the auxiliary flow rate, though the effect is quite small. Having shown this variable to be relatively unimportant, a typical value of 0.8 L min^{-1} was selected, which avoided possible problems with heat from the plasma melting the top of the torch.

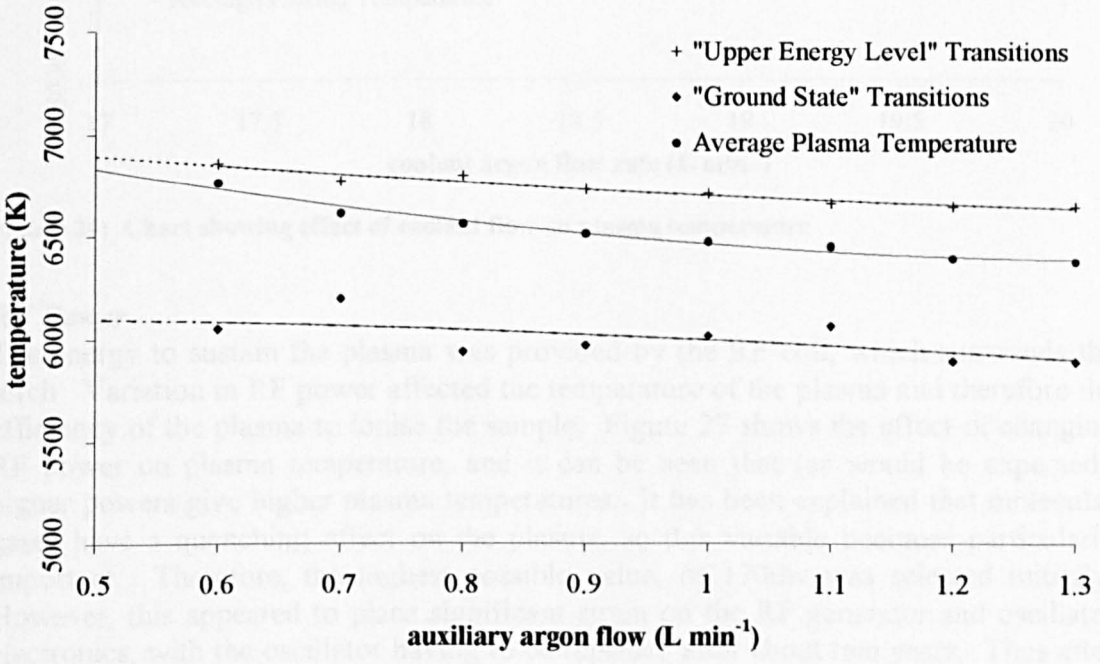


Figure 25: Chart showing auxiliary flow rate against plasma temperature

Coolant Flow

The coolant gas flowed between the middle and outer parts of the plasma torch, and serves two main purposes, cooling the torch wall, and forming the distinctive "flame" shape of the plasma. For gaseous analysis it was necessary to operate the plasma at higher generator power settings and thus there was the need to use higher coolant flows, to avoid melting the torch.

Figure 26 shows the effects of increasing coolant flow rate against plasma temperature. It can be seen that there is an increase in the temperatures of the upper energy levels transitions as the flow rates increase, up to the maximum allowed by the instrument, of 20 L min^{-1}. It should be noted that coolant flows below 17 L min^{-1} could not sustain the plasma under the gaseous measurement operating conditions, i.e. the plasma was effectively "blown out". In order to achieve maximum plasma temperature, and to ensure a stable plasma (by observation of the plasma discharge shape), the highest possible coolant flow rate, of 20 L min^{-1}, was selected. This is significantly higher than the "standard" value for a liquid torch, which is 14 L min^{-1} for this instrument.

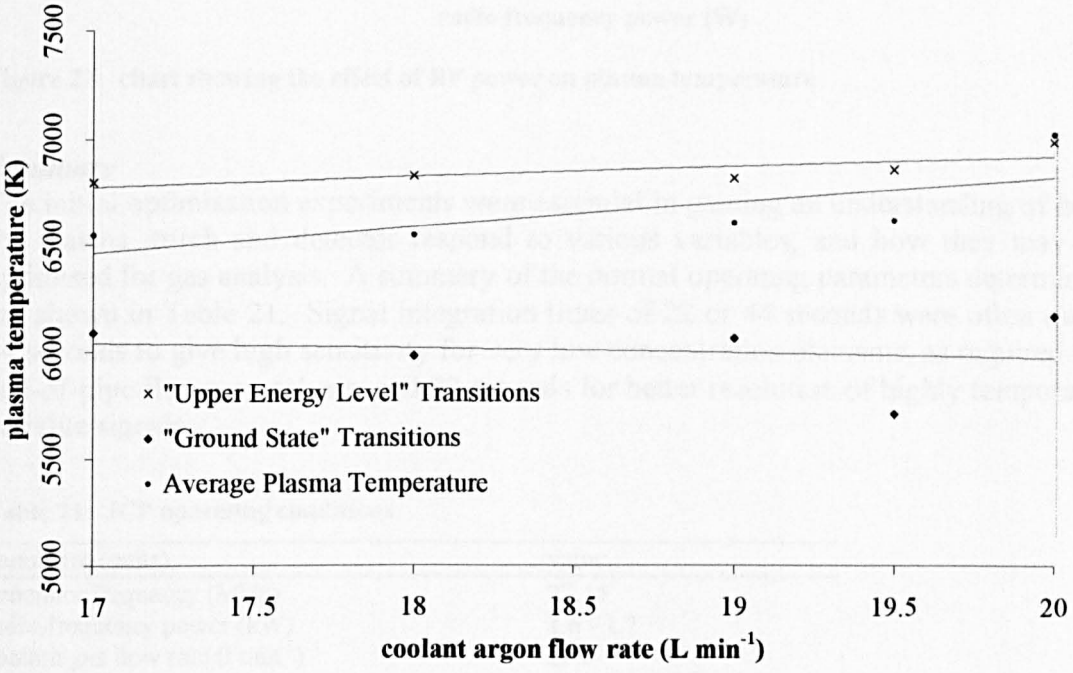


Figure 26: Chart showing effect of coolant flow on plasma temperature

RF Power

The energy to sustain the plasma was provided by the RF coil, which surrounds the torch. Variation in RF power affected the temperature of the plasma and therefore the efficiency of the plasma to ionise the sample. Figure 27 shows the effect of changing RF power on plasma temperature, and it can be seen that (as would be expected), higher powers give higher plasma temperatures. It has been explained that molecular gases have a quenching effect on the plasma, so this variable becomes particularly important. Therefore, the highest possible value, of 1700w was selected initially. However, this appeared to place significant strain on the RF generator and oscillator electronics, with the oscillator having to be replaced after about two years. Thus after this, the power was dropped marginally, to 1600 or 1650w, a compromise between performance and longevity.

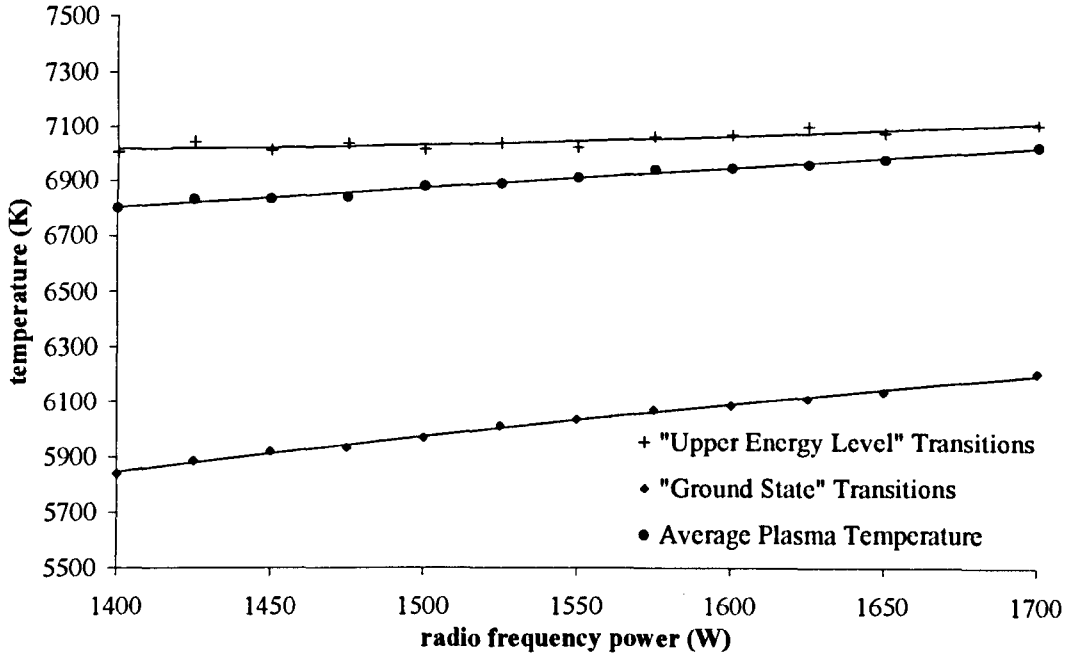


Figure 27: chart showing the effect of RF power on plasma temperature

Summary

The initial optimisation experiments were essential in gaining an understanding of how the plasma, torch and detector respond to various variables, and how they may be optimised for gas analysis. A summary of the normal operating parameters determined are shown in Table 21. Signal integration times of 22 or 44 seconds were often used: 44 seconds to give high sensitivity for very low concentration elements, as required for end-of-pipe flue gas analysis, and 22 seconds for better resolution of highly temporally variable signals.

Table 21: ICP operating conditions

parameter (units)	value
generator frequency (MHz)	27.15
radio-frequency power (kW)	1.6 - 1.7
coolant gas flow rate (l min^{-1})	20.0
auxiliary gas flow rate (l min^{-1})	0.8
nebuliser gas flow rate (l min^{-1})	0.7-0.8
sample gas flow rate (l min^{-1})	0.125 - 0.240
injector tube diameter (mm)	1.8
stabilisation time (s)	15
read time (s)	22 or 44

3.2.2 Systematic Investigation of the Effect of Bulk Gas Matrix on Sensitivity

Having successfully determined a generalised set of optimised ICP-OES conditions for measurement in a gas matrix, the challenge of using the system for measurements of specific elements in a gas stream was investigated. The composition of the bulk gas, notably the carbon dioxide concentration, had been found to have a large effect on some signals, which needed to be accounted for in order to achieve accurate quantification. In some cases, the simplest solution was to select a different line, which suffered less interference from carbon dioxide emissions, or which was quenched less by the presence of carbon dioxide. Thus each analytic line used was carefully checked, to make sure that the effects of the sample matrix did not have an

unacceptable detrimental effect on signal response. In other cases, no line was unaffected by carbon dioxide, and calibrations in a range of gas compositions were required, along with careful use of the background correction facility.

Different gas compositions were investigated. Using the calibration gases and mass-flow controllers, elemental calibration measurements were taken at different carbon dioxide concentrations, to reflect the variable carbon dioxide content of gas samples to be analysed. Artificial dry flue gas mixtures were prepared with carbon dioxide concentrations of 0%, 5%, 10%, and 20%.

For some elements, it was not possible to find an analytic line completely unaffected by changing bulk gas composition. However, with the CCD detector it was possible to set the background corrections so that interferences from carbon molecular and other species were reduced. However, lead in some unfortunate cases to a negative result for some measurements, where the background correction point was not ideal.

Finally, the lines selected needed to reflect the concentrations of different metals which were expected. For example, the most sensitive lines would be required for heavy metals such as Cd, Hg and Tl, but the most sensitive lines for Na or Ca may not be appropriate, due to saturation. Thus careful selection of appropriate lines was required

Having checked the signal, background, and effect of carbon dioxide on various emission lines for many metals, the best available lines were selected for quantitative measurements. Lines were chosen systematically, by examination of the full emission spectrum for the analyte. Single elements standards (1000 ppm) were used to ensure that the signal was due to the analyte, and not the interference of another species in the multi-element standard, or sample matrix. Generally, the most sensitive line without major interference was chosen. However, the emission lines used were under constant review, depending on the requirements for a particular piece of work, so other lines are used for various experiments reported in this thesis. If the line was not a standard analytic line, it also had to be manually added to the software "lines library".

Carbon dioxide concentration was also measured in the gas matrix, by monitoring a carbon line, to allow correction for changing sample matrix composition. Thus a carbon dependence factor for each line could be used to correct the data obtained, depending on the measured carbon concentration. Such correction could either be achieved manually, or by using multi-variable regression analysis within a data handling package, such as Excel. The full results of the systematic line selection for lead and mercury is given in Figure 28 - Figure 31. Table 22 summarises the lines selected by a similar process for "normal" metal measurements in flue gas for other metals.

Table 22 : Emission lines used for early flue gas monitoring

element	wavelength (nm)
carbon	247.856
nitrogen	174.273
oxygen	130.485
argon	430.010
aluminium	396.152
antimony	252.852
arsenic	193.759
cadmium	226.502
chromium	283.563
cobalt	238.892
copper	324.754
iron	259.940
lead	405.785
manganese	257.610
mercury	253.652
nickel	341.476
sodium	589.592
thallium	276.800
tin	242.949
vanadium	309.311

Lead

The emission line generally used for lead was 405.785nm, and the spectrum at this wavelength is shown in Figure 28. The sensitivity of the line is good; the right hand scale is for lead, and the left hand scale for all other elements. There are no significant elemental interferences to this lead line. Nevertheless, to confirm quantification, quantification was frequently confirmed on the 261.418nm or 283.305nm wavelength.

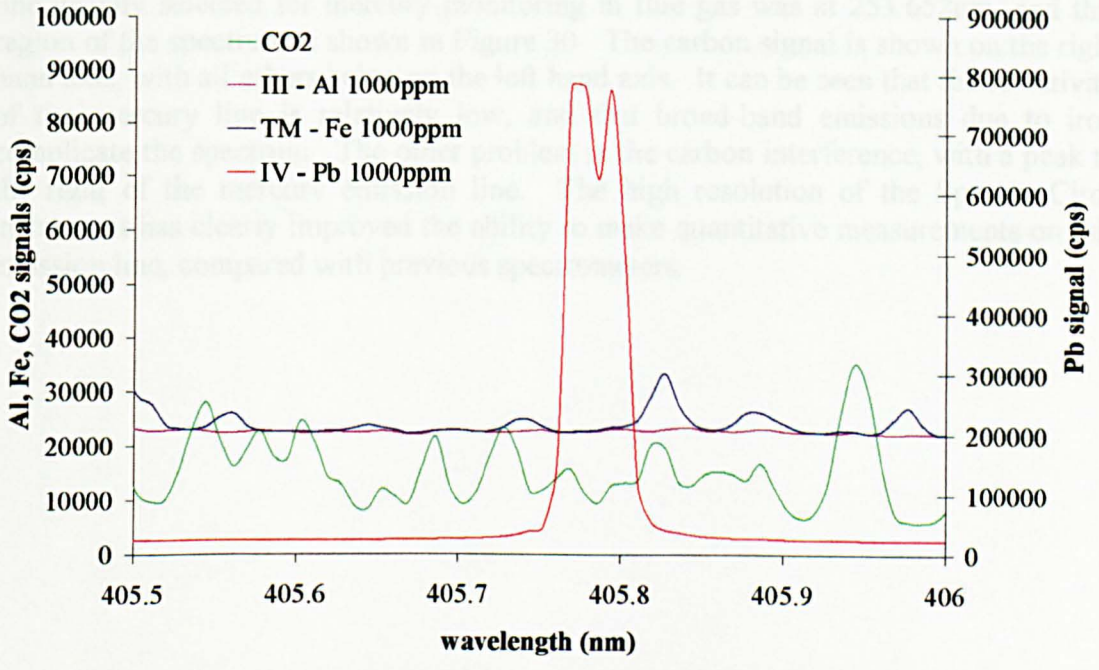


Figure 28: The emission spectra for various elements near the lead I 405.785 nm line

The effect of carbon on the Pb I 405.785nm wavelength is shown in Figure 29. The figure shows that the carbon baseline is quite variable, and although the sensitivity (slope) of the calibrations changes very little with carbon dioxide concentration, the

background (intercept value) increases significantly with increasing carbon. Thus although quantification is perfectly possible on this line, it must be in conjunction with carbon dioxide measurement, so that an appropriate carbon correction can be made.

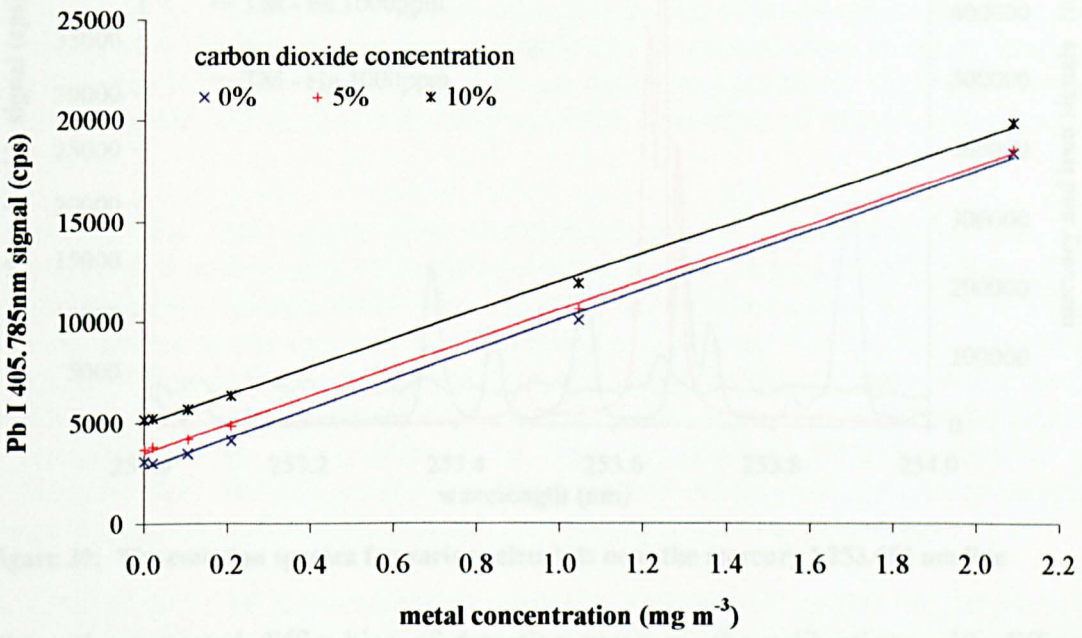


Figure 29: The effect of carbon dioxide on the sensitivity of the Pb I 405.785 emission line

Mercury

Mercury is notorious as an element difficult to quantify using ICP-OES. The emission line usually selected for mercury monitoring in flue gas was at 253.652nm, and this region of the spectrum is shown in Figure 30. The carbon signal is shown on the right hand axis, with all others being on the left hand axis. It can be seen that the sensitivity of the mercury line is relatively low, and that broad-band emissions due to iron complicate the spectrum. The other problem is the carbon interference, with a peak to the right of the mercury emission line. The high resolution of the Spectro Ciros instrument has clearly improved the ability to make quantitative measurements on this emission line, compared with previous spectrometers.

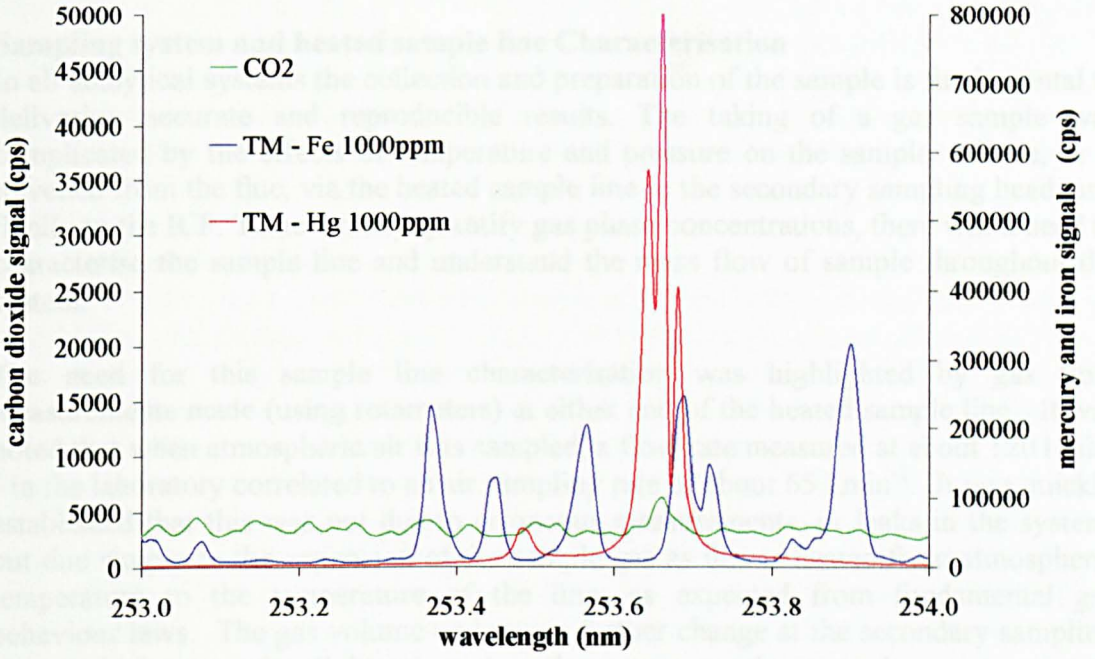


Figure 30: The emission spectra for various elements near the mercury I 253.652 nm line

Given the expected difficulties of detecting mercury, the calibrations with different levels of carbon dioxide, as shown in Figure 31, are really very good. The noise caused by carbon is minimised through careful background correction, and the effect of carbon on sensitivity, though observable, is not problematic. However, the intrinsic low sensitivity of the emission will lead to a relatively high LOD, though still well below the legislative emission limit for mercury. Nevertheless, given the complexity of the emission spectrum in this region, it was considered good practice to confirm any measurements made, via the monitoring of the 194.227nm, 296.728nm, and 435.835nm wavelengths.

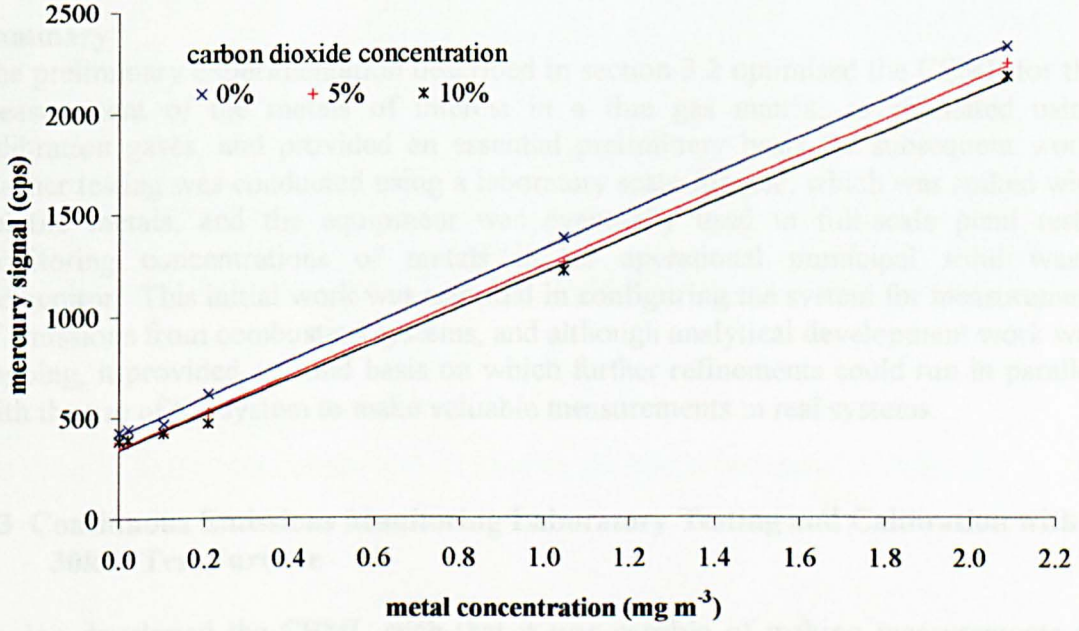


Figure 31: The effect of carbon dioxide on the sensitivity of the Hg I 253.652 nm emission line

Sampling system and heated sample line Characterisation

In all analytical systems the collection and preparation of the sample is fundamental to delivering accurate and reproducible results. The taking of a gas sample was complicated by the effects of temperature and pressure on the sample volume, as it travelled from the flue, via the heated sample line to the secondary sampling head, and finally to the ICP. To accurately quantify gas phase concentrations, there was a need to characterise the sample line and understand the mass flow of sample throughout the system.

The need for this sample line characterisation was highlighted by gas flow measurements made (using rotameters) at either end of the heated sample line. It was noted that when atmospheric air was sampled, a flow rate measured at about 120 l min^{-1} in the laboratory correlated to an air sampling rate of about 65 l min^{-1}. It was quickly established that this was not due to erroneous measurements, or leaks in the system, but due simply to the expansion of the sample gas as it was heated from atmospheric temperature to the temperature of the line, as expected from fundamental gas behaviour laws. The gas volume underwent further change at the secondary sampling stage (which was under slight vacuum), as the temperature began to drop.

A detailed study of the temperature, pressure and volume profile of the sampling system was undertaken. Due to the multiple factors which affect this sampling parameter, the sample enrichment/dilution factor had to be re-evaluated whenever sampling parameters or nebuliser parameters were changed. It was found that when measurements were made on-site, the volume changes down the sample line were small, as the sample line temperature could be matched to the sampling temperature. However, when measuring hotter flue gas from the test furnace, there was significant sample "concentration" due to cooling/contraction, leading to a sample line enrichment factor of about 2.1. Detail of the calculations involved in quantifying gas-phase concentrations between sampling and measurement, which were performed for every different monitoring situation, are given in Appendix 4

Summary

The preliminary experimentation described in section 3.2 optimised the CEML for the measurement of the metals of interest in a flue gas matrix, as simulated using calibration gases, and provided an essential preliminary basis for subsequent work. Further testing was conducted using a laboratory scale furnace, which was spiked with volatile metals, and the equipment was eventually used in full-scale plant tests, monitoring concentrations of metals in an operational municipal solid waste incinerator. This initial work was essential in configuring the system for measurement of emissions from combustion systems, and although analytical development work was ongoing, it provided a sound basis on which further refinements could run in parallel with the use of the system to make valuable measurements in real systems.

3.3 Continuous Emissions Monitoring Laboratory Testing and Calibration with a 30kW Test Furnace

Having developed the CEML such that it was capable of making measurements of metal concentrations in flue gases, a programme of testing was conducted before use for studying volatile metal behaviour in combustion systems. Simple tests were

conducted using flue gas from the furnace as a matrix, into which aqueous standards were introduced in the laboratory, in order to confirm that measurements of metals could be made in flue gases. Subsequently, a full quantitative trial of the whole analytical system was performed using mercury, which was volatilised in the furnace. These tests showed the system to be both sensitive and accurate for measurements in a real combustion system.

3.3.1 Furnace Description

The test furnace was a small steel device with refractory lining. It was heated with an electrically controlled gas oil burner, capable of operating at between 28 and 60 Kw of thermal output, with the burner set for a thermal output of 30-32 Kw. The full operating specifications of this burner are given below. The furnace was located in a laboratory at the Buxton research facility, with the exhaust passing through a vertical chimney for release to atmosphere without any gas clean-up. Gases were sampled by the CEML from a sampling point in the chimney, located on the roof outside the laboratory, about 500mm from the top of the flue. The furnace and chimney are shown in Figure 32. The furnace was fitted with a number of side access ports, one of which was modified to allow the introduction of solid samples, on a stainless steel sample probe. The port allowed spikes of metals and metal compounds to be introduced into the furnace.

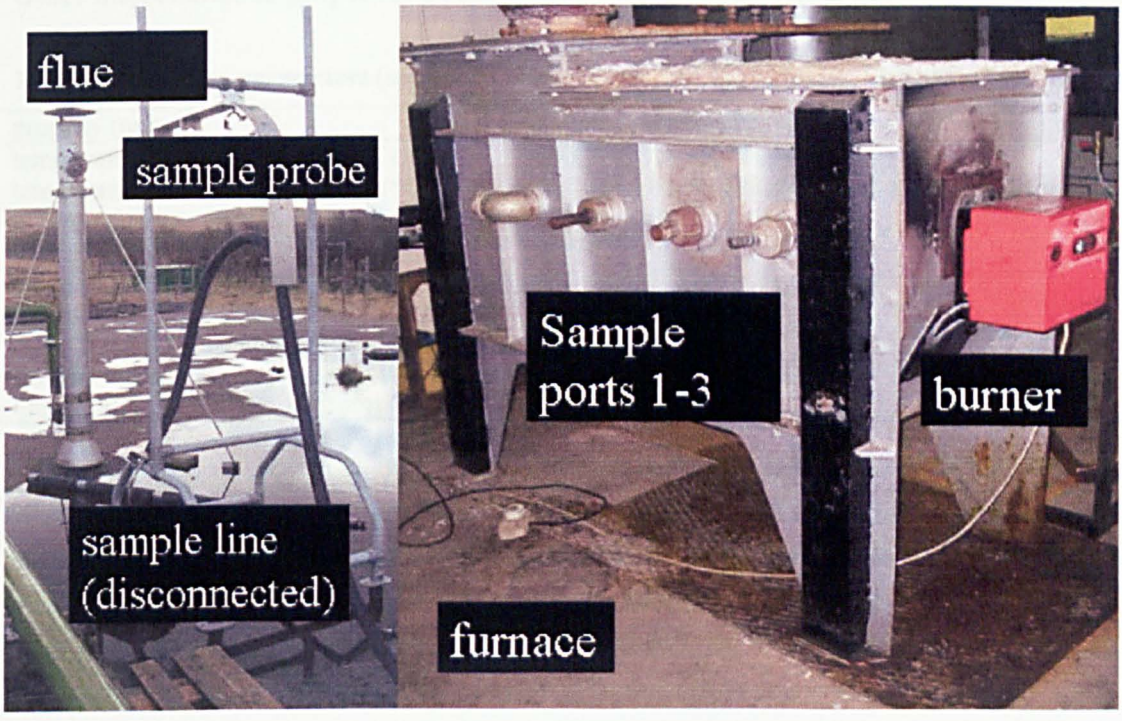


Figure 32: The test furnace and flue

Fuel Oil Characterisation

The main characteristics of the fuel oil used by the burner are given in Table 23.

Table 23: Fuel oil characteristics for the laboratory furnace

property (units)	value	comments
density (kg m^{-3})	853	measured at 15 °C
carbon content (%)	87.3	
hydrogen content (%)	12.5	
oxygen content (%)	0	
nitrogen content (%)	0	
sulphur content (%)	0.2	
ash content (%)	0	
moisture content (%)	0	
net calorific value (MJ Kg^{-1})	41.5	

Burner Characterisation

The main burner operation characteristics are given in Table 24

Table 24: burner characteristics for the laboratory furnace

property (units)	value	comments
fuel consumption (cm^3 min^{-1})	51	= 7.25 E-04 kg s^{-1}
air flow (kg s^{-1})	2.744 x10^{-2}	Excess air = +165%

General furnace properties

Other miscellaneous properties of the furnace are given in Table 25.

Table 25: Furnace parameters (measured after furnace had been run for 2 hours)

property (units)	value	comments
temperature at first access port (°C)	1032	200 mm from burner
temperature at second access port (°C)	740	750 mm from burner, usually used for solids introduction
chimney height (mm)	1950	
chimney ID (mm)	160	
chimney wall thickness (mm)	9	
flue gas temperature at sampling port	350	
flue gas velocity at sampling port (m s^{-1})	2.28	
flue gas flow rate at sampling port (m^3 min^{-1})	2.74	0.0458 m^3 s^{-1}

Characterisation of combustion products

A summary of the experimental and calculated data on the combustion characteristics of the furnace is given below (Table 26). This data was required to calculate the concentrations of metals placed in the furnace, and to calibrate bulk gas measurements from the ICP to known values. Measurements were made using dedicated analysers which were calibrated immediately prior to use.

Table 26: Laboratory furnace flue gas concentrations

property (units)	value	comments
oxygen (%)	13.7	dry gas
carbon dioxide (%)	5.7	dry gas
mass flow rate (kg s^{-1})	2.82x10^{-2}	
Adiabatic flame temperature (°C)	850	

The data given above, in Table 23 - Table 26 were used to obtain the mass-balance results given in Table 27.

Table 27: Mass-balance characteristics of the laboratory furnace

flue gas component	mass flow (Kg s^{-1})	composition (% wt)	composition mol)	(%composition (% dry gas)
H_2O	$8.16x10^{-04}$	2.896	4.651	-
CO_2	$2.32x10^{-03}$	8.240	5.414	5.68
O_2	$3.98x10^{-03}$	14.135	12.771	13.39
N_2	$2.10x10^{-02}$	74.730	77.164	80.93

3.3.2 Initial CEML Flue Gas Monitoring

Experiments were conducted to confirm whether the flue gas from the test furnace was successfully being sampled and measured by the ICP, and whether metals could be measured in that matrix. Elemental emission lines for various elements, including metals and bulk matrix gases (carbon and oxygen) lines were monitored continuously using the test furnace described in 3.3.1 to provide a real flue gas matrix.

Figure 33 shows the results of one experiment. For the first two sections, the furnace was switched off, and the measured oxygen level is high, with the measured carbon level being low, corresponding to the analysis of ambient air. In the third section, the furnace is turned on, and a rise in carbon, and corresponding fall in oxygen signal, is observed, as expected. This confirms that flue gas is actually being sampled successfully, and is reaching the plasma. Qualitatively, the results are as would be expected for air and flue gas, and it confirms that measurements can be made in the matrix.

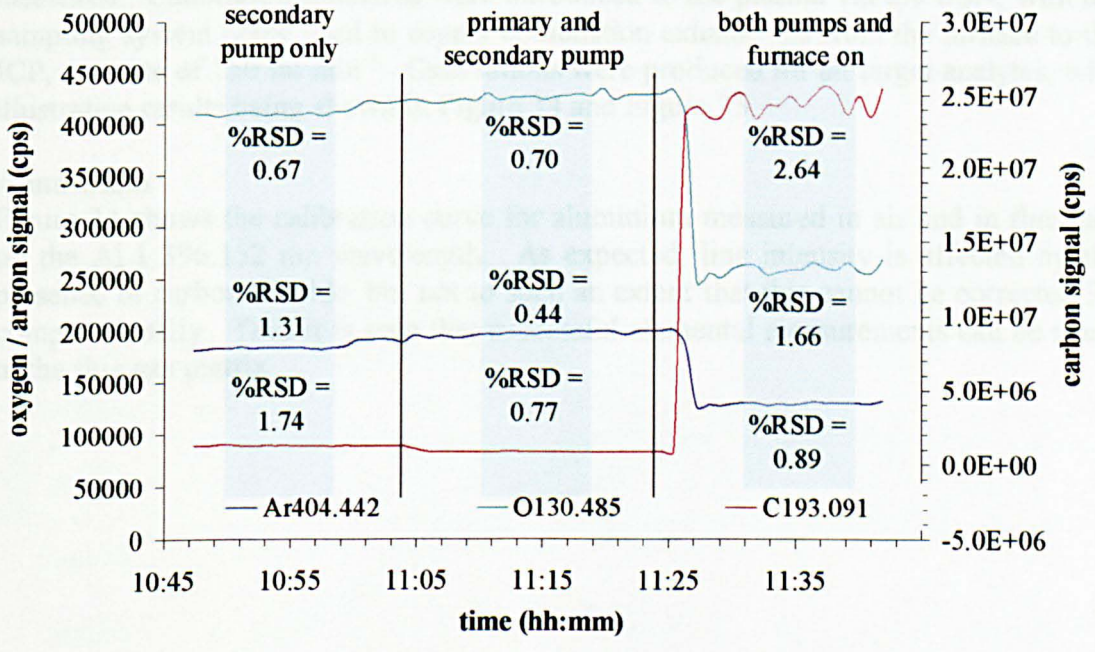


Figure 33: Chart showing the stability of the system under various conditions

To measure stability over an extended period of time, ten consecutive sample points were taken and the relative standard deviation calculated. The area of the sample point is coloured in blue on the chart. With only the secondary pump in operation, it can be seen that percentage relative standard deviation (RSD) of 0.67, 1.31 and 1.74 were obtained for oxygen, argon and carbon, respectively. The values suggest a stable system with low levels of drift.

The second stage of the experiment took measurements with both the primary and secondary pumps in operation. Percentage RSD values for oxygen, argon and carbon of 0.70, 0.44 and 0.77 were obtained. This slight overall improvement is thought to be an effect of the primary pump providing a larger amount of sample to the secondary pump, thus reducing its work and reducing pulsing of the sample gas into the plasma.

The final part of the experiment used the same conditions as above but with the furnace in operation. It can be seen in the chart that the carbon levels increase, and the oxygen and argon levels fell, this relates to the carbon dioxide emitted from the furnace. Oxygen concentrations will fall, due to oxygen consumption by the furnace, and a drop in argon signal results from the quenching effect of increased carbon dioxide in the plasma. The stability was measured as before, with percentage RSD values of 1.66, 0.89 and 2.64 being observed for oxygen, argon and carbon, respectively. These variations are very reasonable, given the expected variation in the furnace performance over time, and the difficulty of making ICP-OES measurements in the gas matrix

From this experiment, it was concluded that the analytical system could operate with a reasonable stability under the operating conditions expected for flue gas monitoring. Further experiments also demonstrated that the analytical system remained stable over longer monitoring periods, of up to several hours.

Having established that reliable measurements could be made in the flue gas matrix, basic experiments were used to show whether the target analytes (i.e. metals) could be measured. Calibration standards were introduced to the plasma via the USN, with the sampling system being used to supply combustion exhaust gas from the furnace to the ICP, at a rate of 150 ml min^{-1}. Calibrations were produced for all target analytes, with illustrative results being shown in Figure 34 and Figure 35.

Aluminium
Figure 34 shows the calibration curve for aluminium measured in air and in flue gas, on the Al I 396.152 nm wavelength. As expected, line intensity is affected by the presence of carbon dioxide, but not to such an extent that this cannot be corrected for computationally. Thus it is seen that successful elemental measurements can be made in the flue gas matrix.

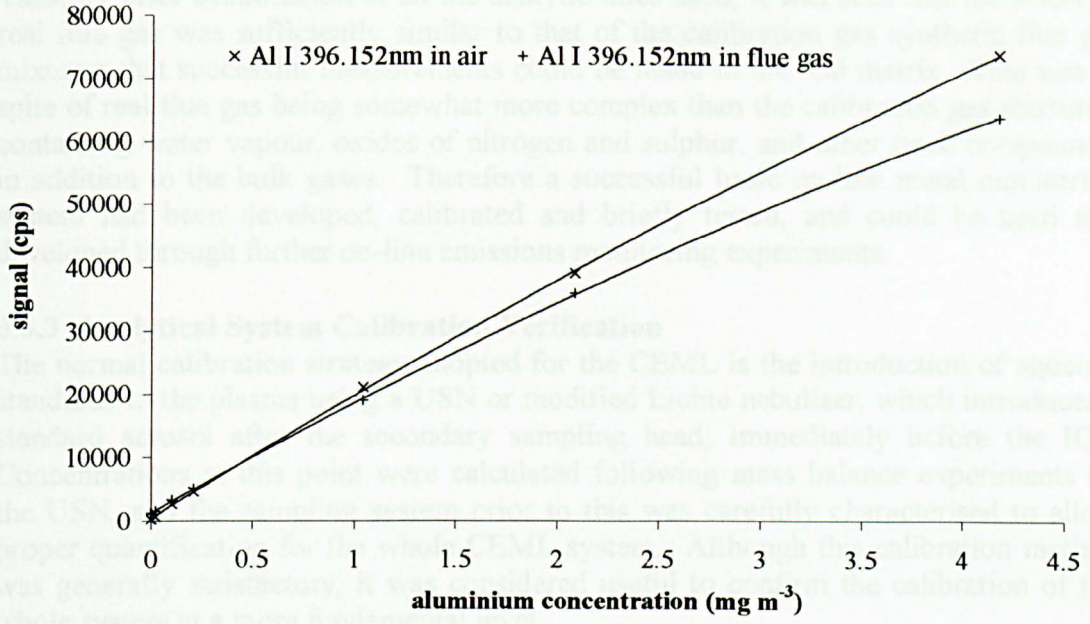


Figure 34: Aluminium calibration curves in air and flue gas, measured on the Al I 396.152nm wavelength

Manganese

Figure 35 shows the calibration curve for manganese, measured on two different emission lines, and in both air and flue gas. Once again, the flue gas matrix has some effect on signal intensity as expected, but good calibration characteristics are still possible. The higher sensitivity of the 257.610 nm line used is illustrated well, showing why it is a better emission line for measurement of trace concentrations of this metal.

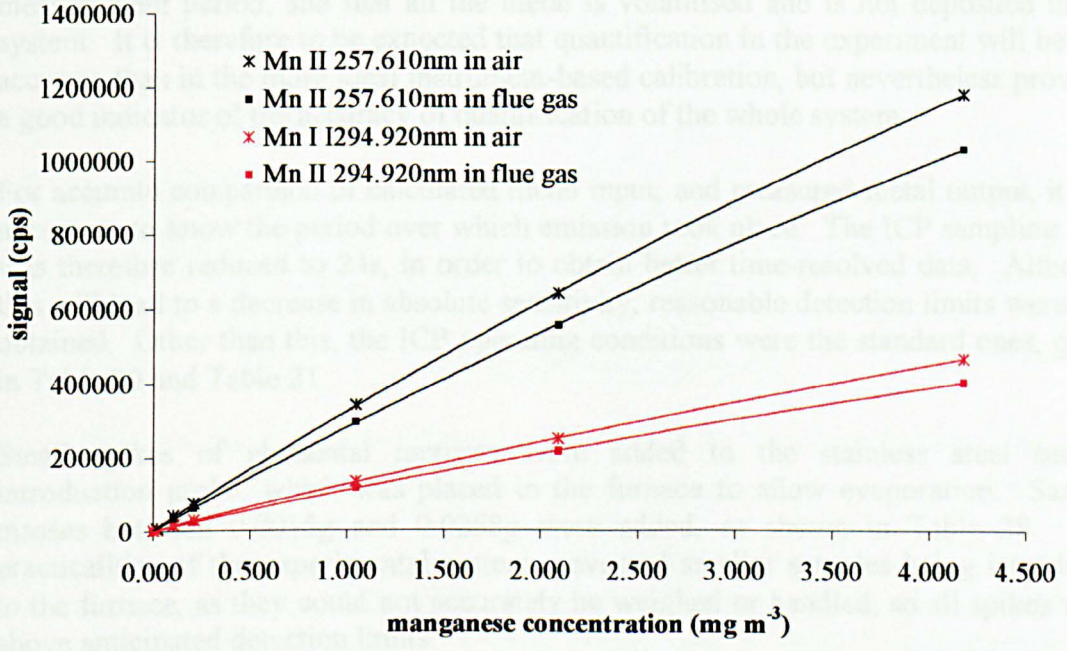


Figure 35: Manganese calibration curves in air and flue gas, measured on two wavelengths

Thus, by brief examination of all the analytic lines used, it was seen that the effect of real flue gas was sufficiently similar to that of the calibration gas synthetic flue gas mixtures that successful measurements could be made in the real matrix. This was in spite of real flue gas being somewhat more complex than the calibration gas mixtures, containing water vapour, oxides of nitrogen and sulphur, and other trace compounds, in addition to the bulk gases. Therefore a successful basic on-line metal monitoring system had been developed, calibrated and briefly tested, and could be used and developed through further on-line emissions monitoring experiments.

3.3.3 Analytical System Calibration Verification

The normal calibration strategy adopted for the CEML is the introduction of aqueous standards to the plasma using a USN or modified Lichte nebuliser, which introduces a standard aerosol after the secondary sampling head, immediately before the ICP. Concentrations at this point were calculated following mass balance experiments on the USN, and the sampling system prior to this was carefully characterised to allow proper quantification for the whole CEML system. Although this calibration method was generally satisfactory, it was considered useful to confirm the calibration of the whole system at a more fundamental level.

Known amounts of volatile metal were placed in the hot furnace, and flue gas emissions were measured using the CEML, following appropriate calibration. Having also completed mass balance studies for the furnace, the amount of metal accounted for in the flue was compared with the known amount added, in order to test the quantification of the whole analytical system, including ICP-OES, USN, and sampling system. This was particularly important for the sampling system, which was had the largest potential for introducing unknown inaccuracies into the measured results, due to possible deposition problems.

It should be emphasised that several assumptions and simplifications are made in using this experimental set-up, for example that volatilisation rate is constant over each measurement period, and that all the metal is volatilised and is not deposited in the system. It is therefore to be expected that quantification in the experiment will be less accurate than in the more ideal instrument-based calibration, but nevertheless provides a good indicator of the accuracy of quantification of the whole system.

For accurate comparison of calculated metal input, and measured metal output, it was necessary to know the period over which emission took place. The ICP sampling time was therefore reduced to 24s, in order to obtain better time-resolved data. Although this will lead to a decrease in absolute sensitivity, reasonable detection limits were still obtained. Other than this, the ICP operating conditions were the standard ones, given in Table 20 and Table 21.

Small spikes of elemental mercury were added to the stainless steel sample introduction probe, which was placed in the furnace to allow evaporation. Sample masses between 0.0015g and 0.0258g were added, as shown in Table 28. The practicalities of the experimental system prevented smaller samples being introduced to the furnace, as they could not accurately be weighed or handled, so all spikes were above anticipated detection limits.

Table 28: Metal spikes added to furnace during experimental run

time from start of experiment (hh:mm:ss)	mass Hg added (mg)
00:10:28	2.9
00:17:00	1.5
00:24:25	1.5
00:32:16	7.5
00:40:33	1.9
00:48:24	12.0
00:56:15	20.6
01:07:11	25.8
01:25:31	6.9
01:33:49	15.1
01:41:15	12.3
01:55:39	14.7

The concentration of metal present in the flue gas of the furnace was measured throughout the experiment using the ICP. The measured gas-phase concentrations were used to calculate the total amount of metal accounted for in the flue gas, and the mass of metal added was compared with the output.

Calibration

The calibration obtained using nebulised aqueous standards is as shown in Figure 36. The linearity and sensitivity observed are excellent.

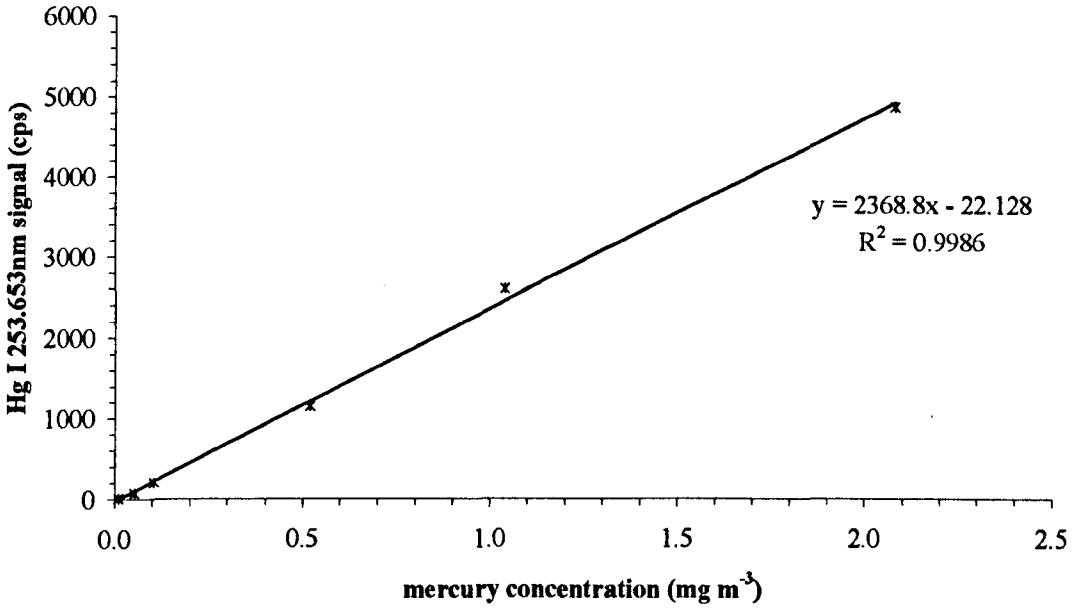


Figure 36: The Calibration Curve for Mercury Measured at the 253.653 nm Emission Line

Continuous Measurements

The emission profile for mercury observed in the flue gas of the furnace during the metal spiking experiment is shown in Figure 37. Twelve emission events are clearly observed, corresponding to twelve spiking events, two of which have been excluded from calculations as outliers (shown in red in Table 28). These outliers may result from impurities in the mercury used, or other uncontrollable variables in the relatively complex experimental configuration. The maximum concentrations on the profile are

approximately 8 mg m^{-3}, for a furnace spike of 25 mg of mercury, and good baseline resolution and stability is observed between the spikes.

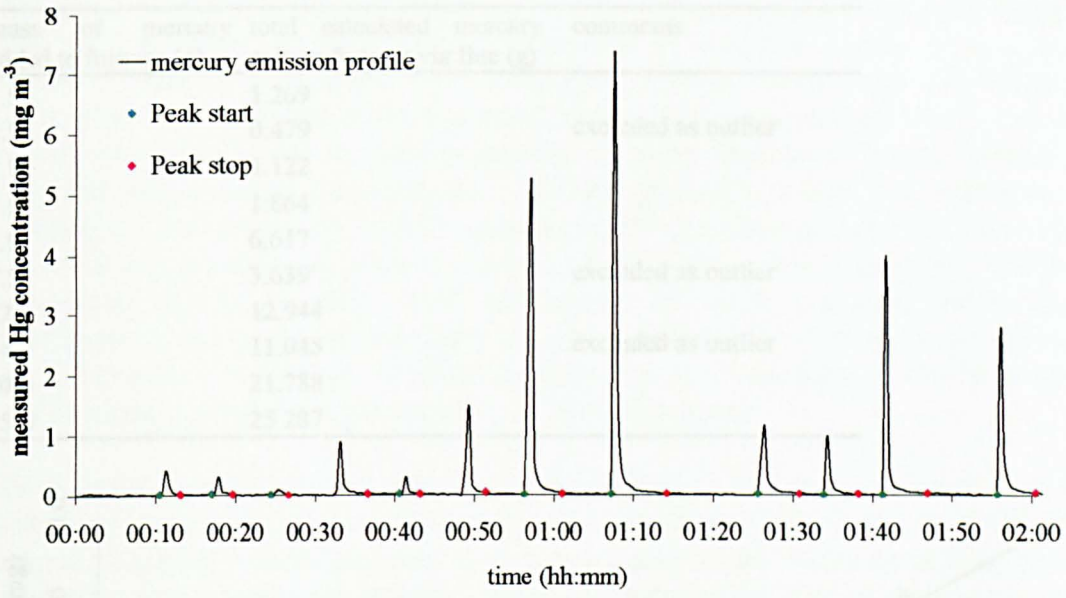


Figure 37: The Emission Profile for Mercury during the Metal Spiking Experiment.

Calculation of Total Mercury in Flue gas based on Measured Concentration

A spiking event in the furnace results in a spike in mercury in the flue gas of up to 8 mg $^{-3}$, and typically lasting 3 – 4 minutes. A measurement of mercury in the flue gas was recorded every 26 – 27s. As the total flow of gas through the test furnace was known, the total amount of mercury released in the flue gas during a single measurement event could be calculated according to the following equation, assuming that emission was constant during each individual measurement period:

$$M_{Hg} = C_{flue} FT \quad (14)$$

Where M_{Hg} is the mass of mercury released during one measurement event (mg), C_{flue} is the measured concentration of mercury in the flue (mg m^{-3}), F is the flow of gas through the flue per second (0.0458 $m^3 s^{-1}$), and T is the time for the measurement (26-27s) The total emission of mercury for the whole spike peak could be calculated using the equation, Where M is the mass (g) of metal measured:

$$M_{Total} = \sum_{PStart}^{PStop} M_{Hg} \quad (15)$$

A comparison between the amounts of mercury added to the furnace and the calculated amount released in the flue gas are shown in Table 29. This data is shown in Figure 38. Agreement between the measured and calculated values is very good. It is generally seen that there is slight over-quantification of the smallest peaks, presumably due to imperfect background corrections for small signals. Large signals are generally well quantified. It may be of concern that within an experiment of 10 data points, 3 are excluded as outliers, showing significant under-quantification. However, given the nature of the experimental setup, this is considered reasonable, and it is seen that where quantification can be classified as "successful", it is actually very accurate.

Table 29: A comparison of mercury additions to the test furnace with calculated mercury emissions from the furnace

mass of mercury added to furnace (g)	total calculated mercury exiting furnace via flue (g)	comments
1.5	1.269	
1.5	0.479	excluded as outlier
1.9	1.122	
2.9	1.864	
6.9	6.617	
7.5	3.639	excluded as outlier
12.3	12.944	
14.7	11.045	excluded as outlier
20.6	21.788	
25.8	25.287	

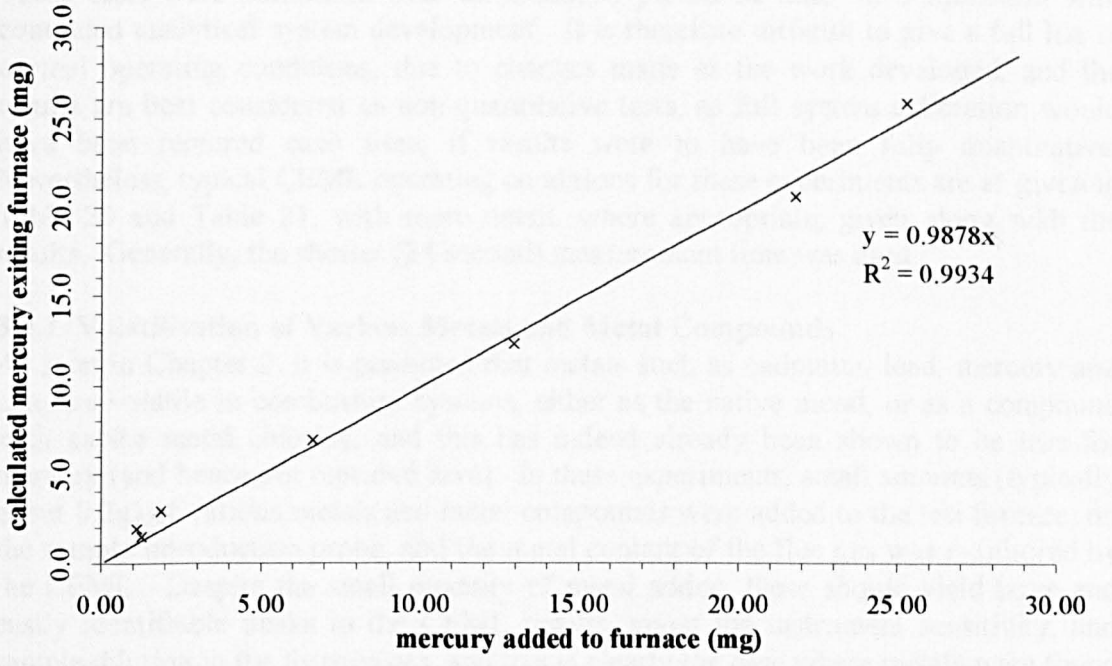


Figure 38: A comparison of mercury additions to the test furnace with calculated mercury emissions from the furnace

This experiment showed that it was possible to quantitatively measure emission concentrations for elements in the gas phase using ICP-OES. It confirmed that the use of a nebuliser to generate an aqueous aerosol standard was an acceptable method of calibration of a gas-phase measurement system. Notwithstanding the significance of the effect of changing gas composition (water, oxygen and carbon dioxide concentrations), the experiment demonstrated that a good correlation could be achieved between measurements of gas phase metal and known metallic input in laboratory conditions, indicating that the CEML was fit for the intended purpose of gas-phase measurements of metal concentrations.

3.4 Use of the CEML to Investigate the Behaviour of Metals in Combustion Systems

The purpose of developing the CEML system for measurements of metals in flue gases was to investigate the volatilisation behaviour of different metals in combustion systems. Various experiments were conducted with the CEML and test furnace, in order to test the operation of the analytical system, and to investigate the volatilisation of different metals, and to confirm whether existing theories of metal volatilisation reflected experimental observations. It was generally found that elements and compounds predicted to be volatile were detected in the flue gas, and that non-volatile elements and compounds were not, though there were a few exceptions, which are considered in the results. This programme of work not only aided system development, but provided extremely valuable verification of existing predictions of metal behaviour in thermal systems, and showed that reactions in the burning bed could enhance or suppress the volatility of particular metals.

These tests were conducted over an extended period of time, in conjunction with continued analytical system development. It is therefore difficult to give a full list of normal operating conditions, due to changes made as the work developed, and the results are best considered as non-quantitative tests, as full system calibration would have been required each time, if results were to have been fully quantitative. Nevertheless, typical CEML operating conditions for these experiments are as given in Table 20 and Table 21, with more detail, where appropriate, given along with the results. Generally, the shorter (24 second) measurement time was used.

3.4.1 Volatilisation of Various Metals and Metal Compounds

As seen in Chapter 2, it is predicted that metals such as cadmium, lead, mercury and zinc are volatile in combustion systems, either as the native metal, or as a compound such as the metal chloride, and this has indeed already been shown to be true for mercury (and hence not repeated here). In these experiments, small amounts (typically about 0.2g) of various metals and metal compounds were added to the test furnace, on the sample introduction probe, and the metal content of the flue gas was monitored by the CEML. Despite the small quantity of metal added, these should yield large and easily identifiable peaks in the CEML results, given the instrument sensitivity, and sample dilution in the furnace gas, and this is clearly the case where metals were found to be volatile. A list of the species added to the furnace is given in Table 30.

Table 30: Metals and metal compounds added to the laboratory furnace to assess volatility

species	mass (g)	boiling point (°C) (Weast et al., 1988)	presence in gas stream expected	comments
Al	0.5g	2467	no	
Al_2O_3	1.0g	2980	no	
Ca	0.6g	1484	no	
Cd **		765	yes	
$CdCl_2$**		960		
Cr	0.7g	2672	no	
Cu	0.5g	2567	no	
$CuCl_2$	0.2g	993*	no	decomposes to CuCl
CuCl	0.2g	1490	no	
Fe	0.2g	2750	no	
$FeCl_2$	0.2g	NA		melts at ~670, sublimes
KOH	0.2g	1320	no	
Mg	0.5g	1107	no	
NaOH	0.2g	1390	no	
Ni	0.9g	2730	no	
$NiCl_2$	0.2g	973*		sublimes
Pb	2g	1740	no	
$PbCl_2$	0.2g	950		
Sn	1.0g	2260	no	As Sn/Pb alloy
$SnCl_2$	0.2g	652	yes	
Zn	0.7	907		
$ZnSO_4$	0.2g	600*		decomposes
$ZnCl_2$	0.3g	732	yes	

3.4.2 Volatile Products from Reactions of Metals in the Combustion System

It has been explained in the literature review (Chapter 2) that the burning bed of an incinerator is a complex reacting system, and that reactions of metals or metal compounds with other species on the burning bed may enhance or suppress volatility. Using the experimental system available; with the laboratory furnace to provide a combustion environment, and the CEML to monitor gaseous products, studies were conducted into whether reactions could occur between different species on the bed, helping to increase understanding of how metals behave in combustion systems.

A list of the different reactant combinations added to the furnace, along with a brief explanation of the purpose of each experiment, is given in Table 31. Obviously, the list is not exhaustive, but the results of these experiments served to illustrate how complex the combustion system was, and how important it was to consider a range of species and reactions of each metal being studied.

Table 31: Reactants added to the laboratory furnace to assess burning-bed volatilisation reactions

species 1	species 2	expected products	comments
Sn	$HONH_3Cl$	$SnCl_2$	non-metallic source of HCl
Sn	NH_4I	SnI_2	source of HI
Sn	I_2	SnI_2	source of I_2
Sn	S		
Sn	PVC	$SnCl_2$	"real" source of HCl
Sn	PVC	$SnCl_2$	with S also present, to test effect of competing anions
Pb	$HONH_3Cl$	$PbCl_2$	
Pb	$ZnCl_2$		to test "competition" for anions between metals
Pb	$SnCl_2$		to test "competition" for anions between metals
Pb	$NiCl_2$		to test "competition" for anions between metals
Pb	$CuCl_2$		to test "competition" for anions between metals
Al	$HONH_3Cl$		to see if HCl source can volatilise "non-volatile" metals
Al	$ZnCl_2$		to see if volatile salts can volatilise "non-volatile" metals
Al	$SnCl_2$		to see if volatile salts can volatilise "non-volatile" metals
Al	$NiCl_2$		to see if volatile salts can volatilise "non-volatile" metals
Al	$CuCl_2$		to see if volatile salts can volatilise "non-volatile" metals
Zn	$HONH_3Cl$	$ZnCl_2$	to see if HCl source can volatilise "non-volatile" metals
Zn	$SnCl_2$		to test "competition" for anions between metals
Zn	$NiCl_2$		to test "competition" for anions between metals
Zn	$CuCl_2$		to test "competition" for anions between metals
Zn	$PbCl_2$		to test "competition" for anions between metals

3.5 Continuous Emissions Monitoring at a Large-Scale Municipal Solid Waste Incinerator

A robust system had been developed which was capable of making unique accurate, and reliable measurements of concentrations of metals in flue gases (as vapours and as small particulates). The CEML was used for two campaigns of measurement at a commercial MSW incinerator. The first study investigated the concentration of metals in the flue gas emissions to atmosphere, and the second examined the concentrations in the raw flue gas, prior to gas clean-up. Each on-line study was supported by a series of conventional measurements of metal concentrations in solid incinerator residues, which helped to confirm the accuracy of the new on-line measurements. Although the study of emitted flue gas was technically much less demanding, it revealed far less about the fluctuations in metal volatilisation from the burning bed, and the study of a highly contaminated, dusty un-cleaned flue gas gave a far more useful insight into the fluctuating concentration of different metals released from the burning bed.

For each study, the CEML was transported to the plant by lorry and for the duration of the sampling regime was left on the trailer, which is seen in Figure 39. The plant provided power and water to the CEML, and liquid argon was supplied on-site by Cryoservice (Worcester, UK). After arrival at the plant, the CEML was powered up and the ICP-OES was allowed to equilibrate for 24 hours before use. Each measurement campaign lasted one week, with 2 days before for set-up and 1 after for preparation for transport, with one study being completed in December 2002, and the second being completed in July 2004.

Figure 39: CEML arrival at the MSWI prior to installation of steps

3.5.1 Description of Industrial Plant

The test site selected for this work was a mass-burn MSWI plant, which is shown schematically in Figure 40. The plant had 2 lines, each incinerating up to 12 tonnes of waste per hour, with an average throughput of approximately 10 tonnes per unit per hour. The grate was a Martin reverse reciprocating grate, and the furnace walls were water cooled, providing heat to the energy recovery system. Furnace temperature was measured by the plant operator using two thermocouples, one on either side of the furnace. The plant was operated so as to maintain the temperature between 850°C and 1100°C, and with excess combustion air leading to an oxygen level between 6% and 14%, measured in the radiation shaft. The combustion chamber was followed by the energy recovery boiler, and an economiser, resulting in a final flue gas temperature after the economiser averaging 130°C. The heat generated by the process was used to generate 13 MW of electricity, and also provided heating to local buildings, through a district heating system. Hot flue gases were used to generate steam for the energy recovery system, through radiative heating of the water walls of the combustion chamber and superheater, and by convective heating of the multi-tubular heat exchanger and economiser.

Flue gas treatment comprised of a dry scrubbing system using hydrated lime to control acidic gas emissions, and activated carbon to trap heavy metals and organic micro-pollutants. Fabric filters were used to collect the fly ash and scrubber products, and were designed to remove particulate matter down to a minimum of 5μm. The emitted flue gas was continuously monitored beyond the fabric filter by the plant operator, for temperature, and concentrations of CO, SO_2, NO_x, HCl, O_2, H_2O, and dust, using a CODEL system (CODEL International Ltd, Bakewell, UK).

Two flue gas sampling points were used in the course of this work. Cleaned flue gas measurements were made beyond the fabric filters, in a straight section of ducting, before the ID fan, and the mixing of the flue gases from the two lines before the stack. Un-cleaned flue gas was sampled after the economiser, and before the sorbent injection of the flue gas clean-up system. Each sampling point was fitted with a standard 4" BSP port in a vertical section of ducting, well away from any bends or other

obstructions in the flue, with the port for "clean" gas being the one used for the environment agency extractive emissions testing. The sampling points are indicated on the schematic diagram, Figure 40. The CEML sample train was connected to one of these ports, at which point the ducting measured about 0.9m x 0.9 m, and continuous on-line emission monitoring of flue gas was undertaken.

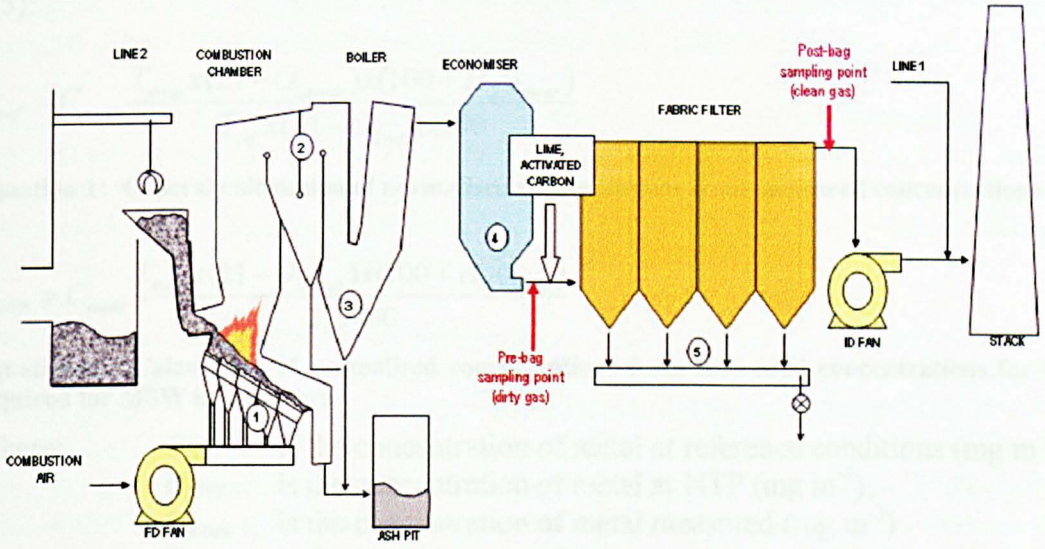


Figure 40: Schematic diagram of the incinerator plant, showing the sampling locations

During the combustion trials, the plant was burning unsorted municipal waste, collected from homes and businesses in the surrounding area. Information on the composition of this waste is extremely difficult to obtain, with no specific information available on elemental composition, although it is known that the average calorific value of the waste delivered to the plant in the year 2001 was 10.50 $MJkg^{-1}$. General estimates of the composition of municipal waste were given in the literature review (Chapter 2). Ultimately, given the difficulties of obtaining accurate, consistent, and representative data on waste composition, given its inhomogeneity and seasonal and regional variability, it might be considered better to use the analyses of incinerator residues to back-calculate the incoming waste compositions, along with the new on-line monitoring data presented, give a better indicator of the composition of the original waste than has previously been available.

Data Collected

In addition to the data collected using the CEML, the measurements made by the plant during the monitoring time were made available. Data was collected for furnace conditions (temperature and oxygen), measured at the top of the radiation shaft, as were temperatures of the flue gas before and after the economiser. The full set of emission data, recorded by the CODEL system, was obtained for cleaned flue gas, following the bag filters. At this point, temperature, oxygen (%) and flow (cubic metres per second), and data on sulphur dioxide, hydrogen chloride, particulate, and other emissions were recorded. These measurements were made in the line 1 ducting, immediately prior to the point where the gases from the two incinerator lines meet at the base of the stack. The bulk composition, temperature and flow data were used to normalise the CEML results to standard reference conditions, and to see how metal emissions changed with plant conditions. In order to simplify comparison of data from different sources (i.e. plant and CEML), one value was used per minute, with the last

data point from any one minute being used in the event of multiple measurements within the period.

Plant recorded data had been normalised to 11% O_2, dry gas, 1 atmosphere, 273 K. Accordingly, CEML measured data was converted to the same conditions using the general correction (14), which for these specific reference conditions simplifies to (15):

$$C_{ref} = C_{meas} \frac{T_{meas} x(21 - O_{2meas}) x(100 + H_2 0_{meas})}{T_{ref} x(21 - O_{2ref}) x100} \quad (16)$$

Equation 1: General calculation of normalised concentrations from measured concentrations

$$C_{NTP} = C_{meas} \frac{T_{meas} x(21 - O_{2meas}) x(100 + H_2 0_{meas})}{273000} \quad (17)$$

Equation 2: Calculation of normalised concentrations from measured concentrations for NTP required for MSW incinerators

Where:

C_{ref}	is the concentration of metal at reference conditions (mg m^{-3})
C_{NTP}	is the concentration of metal at NTP (mg m^{-3})
C_{meas}	is the concentration of metal measured (mg m^{-3})
T_{meas}	is the temperature at the measurement point [taken to be the plant economiser outlet temperature] (K)
T_{ref}	is the reference (NTP) temperature (K)
O_{2meas}	is the measured flue gas oxygen content at the measurement point [taken to be the plant measured oxygen measured beyond the bag filters] (%)
H_2O_{meas}	is the measured flue gas water content at the measurement point [taken to be the plant measured water measured beyond the bag filters] (%)

Additional Samples Collected

During on-site continuous emissions monitoring experiments at the MSWI, samples of bottom ash, and APC residue were collected daily. During the monitoring of un-cleaned flue gas, fly ash (before lime addition) was collected in the cyclone, and this was also preserved. These samples were analysed for metal content, allowing further information to be gathered on the distribution of metals in the furnace, and so allowing some confirmation of the on-line measurements made by the CEML.

Although a formal sampling strategy was not adopted, care was taken to ensure consistent methods were used. Samples of bottom ash and APC residue were taken at about the same time each day, between 3:00 and 4:00 pm. It is appreciated that the collection protocol adopted would not fully satisfy the rigorous requirements to ensure representative sampling (Van Der Sloot et al., 1997), but it was the best achievable in the conditions encountered, and the samples size was large enough that they should have been reasonably representative of the bulk material.

Bottom ash was collected beyond the quench pit, from the grating which was used to separate bulky items from the main ash. About 10 kg was collected, with large, identifiable items such as masonry or bulk ferrous metal being rejected from the sample at the point of collection (anything over about 200mm in any dimension). At

this point the residues from the two incinerator lines were mixed. Samples of about 5kg of APC residue were collected from an access point in the transport system for used lime/APC residue, before mixing of the residues from the two lines. Thus collection was as close as possible to "fresh" APC residue, prior to damping with water. Fly ash, which was collected in the BCURA sampling probe during un-cleaned flue gas analysis, was removed periodically from the cyclone, and amounted to about 3-5 kg per working day (8-10 hour monitoring period). Collected samples were stored in sealed plastic containers at room temperature until analysis.

3.5.2 Analysis of Solid Residues from Municipal Solid Waste Incineration

The formal method used in the laboratory for the analysis of solid incinerator residues is given in Appendix 2. This method, which was developed internally from information given in the relevant British/EU and American standards (British Standard EN13657:2001, 2001), is summarised below.

Pre-Preparation of Laboratory Samples

Given the large particle sizes encountered, particularly for bottom ash, samples were ground prior to acid digestion using a cross-beater rotary mill (Model 16-150, Glen Creston Ltd, Middlesex, England), in order to reduce inhomogeneity. The raw sample was mixed, coned and quartered, with half of the sample being retained, and half being ground until it was small enough to pass through a 0.5mm mill mesh. For samples with a large initial particle size, they were first ground to pass through a 5mm mesh. Although the upper particle size limit was therefore 0.5 / 5mm respectively, the majority of the resultant particles were much smaller than the mesh screen in the mill, and sample homogeneity was much improved. The resulting residues were mixed, and stored again in sealed plastic containers. For convenience of handling, laboratory sub-samples were taken in 50ml polypropylene sample tubes for analytical purposes.

Digestion Method

Two strong acid digestion methods were used, although both were digestions using a mixture of concentrated hydrochloric and nitric acids (aqua regia). The first was a conventional thermal digestion, where the samples were boiled in the acid mixture in an electrical heating unit. The second was a microwave-assisted sealed tube digestion, which had the advantage of offering more "harsh" digestion conditions (and hopefully better digestion as a result), but was only capable of using a smaller sample.

It is appreciated that the aqua regia digestion procedure employed will not give a "true total content" for some metallic elements, notably silicon, aluminium, and possibly calcium. However, the use of more aggressive reagents, such as a hydrofluoric acid / aqua regia / perchloric acid mixture was avoided due to the highly corrosive reagents involved, and the known drawbacks of this technique, i.e. the possible loss of Cr, Si, Ag, As, B, Ca, K, Mo, Sb, Se and V leading to poor quantification (Van Der Sloot et al., 1997). Although not perfect, it is believed that the aqua regia digestion used presents the best "compromise conditions" for general analysis, given that the main interest was in heavy and trace metal content, not in bulk "inert" constituents. It should be noted that the method is not appropriate for mercury analysis, due to the risk of loosing mercury vapours at the temperatures involved in the digestions.

Thermal Digestion

For the thermal analysis, 2.0 g samples of solid were weighed accurately on a 4-figure balance, and placed in 350 ml pyrex tubes of a Büchi 6-Sample Digester (Fisher

Scientific, Loughborough, UK). 15ml of hydrochloric acid was added, followed by 7.5ml of nitric acid, and the samples were boiled for 2 hours. The temperature was maintained such that a reflux was maintained on the tube sides, which were air cooled, and the sample volume was conserved. The samples were periodically agitated, to ensure that the whole of the solid sample was exposed to the acid mixture.

Microwave Assisted Digestion
Samples were digested using an Anton Paar Multiwave 3000 microwave digester (Anton Paar, Hertfordshire, UK). 8 samples were digested simultaneously. 0.5g of solid was weighed accurately on a 4-figure balance, and placed in the digestion vessel. 6 ml of nitric acid was added, followed by 1ml of hydrochloric acid. The samples were placed in the microwave, and were microwaved at 1400w, ramped linearly from zero over 5 minutes, and held at full power for 20 minutes.

Sample Analysis By ICP-OES
Digested samples (from either digestion method) were allowed to cool, filtered or centrifuged to remove or compact any insoluble material, and diluted to 50 ml with de-ionised water. These samples were collected in 50ml polypropylene tubes, and were stored at room temperature prior to analysis by ICP-OES. For major constituents (e.g. aluminium, calcium, sodium), 10-fold, 100-fold or even 1000-fold dilution of the initial sample was required, to obtain concentrations in the measurable range.

The samples were analysed for aqua-regia soluble metal content using the Spectro Ciros ICP-OES in the CEML, which is described in 3.1 . The ICP was fitted with the standard torch for liquid analalyses, and a modified lichte pneumatic nebuliser. The system was calibrated using 0, 0.01, 0.1, 0.5, 1, 5, and 10 ppm multi-element standards (Bernd Kraft GmbH Salze & Lösungen, Duisburg, Germany). To prevent concentrated samples contaminating subsequent analyses, the most dilute (1000 or 100-fold diluted) form of each sample was analysed first, followed by the 10-fold diluted, and then the undiluted. Between different samples, 10% HNO_3 was run through the ICP for two minutes, to remove residual sample contamination. The main ICP operating parameters, which are standard conditions for liquids analysis, are given in Table 32.

Table 32: ICP operating parameters for solids analysis

parameter (units)	value
generator frequency (MHz)	27.15
power RF (kW)	1.4
plasma gas flow rate (l min^{-1})	12.0
coolant gas flow rate (l min^{-1})	1.0
nebuliser gas flow rate (l min^{-1})	0.8
injector tube diameter (mm)	0.8
stabilisation time (s)	15
read time (s)	12-24

Some of the solid samples were also analysed by an independent laboratory (SUMAC, University of Sheffield), to provide verification of the data obtained. A full method is not available for the samples digested externally, which were provided un-prepared to that laboratory, but is known to have consisted of an acid digestion, and ICP-OES analysis.

3.5.3 Measurement of Atmospheric Emissions

The CEML was connected to the plant sample port with the 40m heated sample line. The path of the heated sampling line, from the port, to the CEML, is shown in Figure 41. Compared with the complexity of measuring metal concentrations in the un-cleaned gas, measurements of the emitted flue gas was relatively straightforward. Gas was isokinetically sampled from the 4" BSP sample port after the bag filters, (described in section 3.5.1) using the 40m-heated sampling line and BCURA probe (described in section 3.1.4) (with smallest tip fitting). The use of the cyclone was not necessary as the gas was essentially free of large particulates. The sample line was operated at a temperature of 200°C. A sub-sample was taken, using a double head, out of phase, peristaltic pump via a secondary sampling stage at 0.24 L min^{-1}. The sampling port is shown in Figure 42.

Other than this difference at the sampling head end of the analytical system, the CEML was essentially the same as for un-cleaned gas, described in section 3.5.4. The nebuliser and ICP-OES conditions differed slightly, as shown in Table 33 and Table 34. However, due to the fact that the gas volumes (sample and nebuliser argon) differ significantly between the two experiments, and also because the USN performance was significantly changed following a major overhaul, the concentrations of the 0-10 ppm standard solutions corresponded to 0 – 2.1 mg m^{-3} in the gas phase, and thus were significantly different from the subsequent work, where sensitivity was much improved. Nevertheless, the concentrations in each case accurately represent the gas-phase concentration of the standards reaching the ICP.

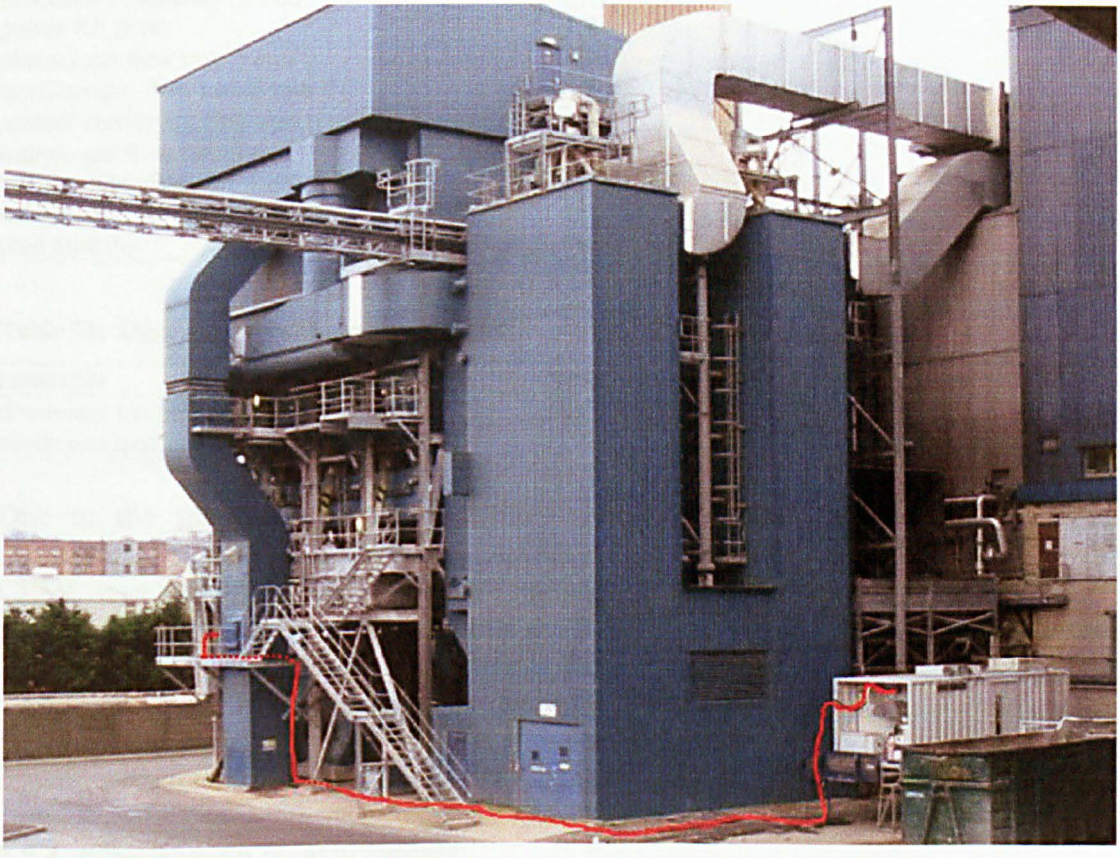


Figure 41: The path of the heated sample line, from the plant duct to the CEML

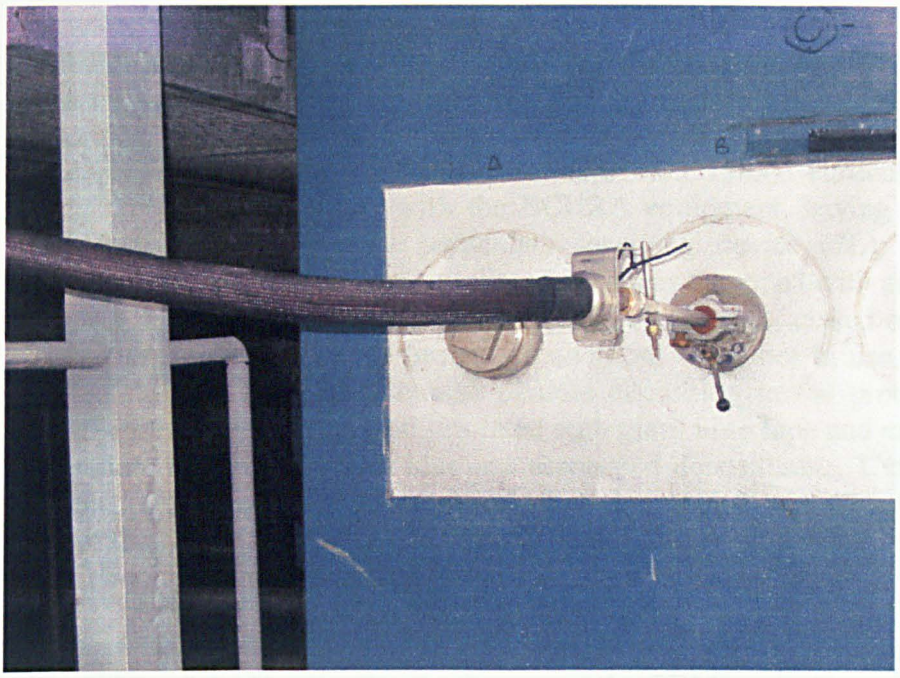


Figure 42: The heated sample line and probe, connected to the flue gas duct sampling point.

Table 33: ICP operating parameters for flue gas monitoring

parameter (units)	value
generator Frequency (MHz)	27.15
power RF (kW)	1.7
plasma gas flow rate (l min^{-1})	20.0
auxiliary gas flow rate (l min^{-1})	0.8
aerosol carrier gas flow rate (l min^{-1})	0.7
sample gas flow rate (l min^{-1})	0.24
injector tube diameter (mm)	1.8
stabilisation time (s)	15
read time (s)	44

Table 34: Operating conditions for the USN

parameter	target Value	typical High Value	typical Low Value
desolvator temperature	160° C	161° C	158° C
condenser temperature	2° C	2.5° C	1.5° C

Due to the relatively simple analytical matrix, and low analyte concentrations, quantification, and long-term system stability were very good in clean flue gas. The CEML was therefore left running for long periods (in excess of 24 hours), and this is reflected in longer uninterrupted results profiles. Other than this, the only significant point of note is that the air conditioning was damaged during transportation to the plant, and thus the laboratory was operated with electric heaters, and without air cleaning, but nevertheless, successful measurements were made. The results of the experiments detailed above are given in Chapter 5.

3.5.4 Pre-clean-up measurements

Sample Train

The CEML was connected to the plant sample port with the 40m heated sample line. The use of the adapted BCURA sampling probe (section 3.1.4), ensured isokinetic

sampling (as far as possible), and removed large particulates (dust and grit). The BCURA sampling device, which consisted of a sampling tip, sampling probe, mini-cyclone, isolation valve, and outlet to heated sample line, was assembled and used according to the instructions (BCURA, 1996), which are in accordance with the appropriate British Standard (British Standard 3405, 1983). Particulates were removed using the cyclone supplied with the BCURA equipment, having been fitted with a custom-made large-capacity particulate receiving device (2L), to allow use for extended periods of use. The sampling device was equipped with an isolation valve so that the sample probe could be left in the flue overnight, closed off, to minimise air ingress or deposition on the probe. In addition, when not in use, the probe tip was rotated through 180°, to minimise particle deposition in the probe tip. The entire sampling train was lagged and insulated with glass fibre tape and expanded foam pipe insulation, to minimise heat loss and associated depositions. The laboratory heated sample line was maintained between 150° C and 160° C throughout the week, slightly higher than the economiser temperature, in order to minimise depositions, which were problematic within the sampling train.

The static pressure drop in the flue was 2.5 kN m^{-3}, and the pressure differential across the cyclone 0.8 kN m^{-3}. Due to the use of the CEML primary pump, rather than the original BCURA pump, the cyclone pressure drop was rather low, so the smallest sample head (0.0002 m^2) was selected, according to the BCURA manual (BCURA, 1996). This gave slightly sub-isokinetic sampling, but was as near as possible to isokinetic.

Given that the cyclone was put in place to remove particles over 10 μm, and that the remaining gas sample should only contain smaller particles and vapour, the sampling methodology was adequate, as deviations from isokinetic conditions have minimal effect on the smallest particles, i.e. less than 5 μm (Clarke, 1998), which will actually reach the ICP and undergo effective analysis (Trassy, 1996), and in any case, have the highest concentrations of volatile metals (Greenberg et al., 1978). A traverse of the stack was not conducted, as once more the distribution of such particles through the stack is reasonably consistent, and temporal variations in the on-line data would have been complicated by the introduction of a further variable.

Due to technical difficulties with the equipment, only one channel of the 2-head out of phase peristaltic pump was used, at maximum speed, so corresponding to an analytical sample flow of 125 ml min^{-1}. This was mixed at a t-piece connector with nebuliser argon flowing at 0.5 l min^{-1}, and was transported through the USN to the ICP. The USN was operated nebulising 10% HNO_3, (supplied through one 0.89 mm bore peristaltic pump tube) to standardise normalise sample water content during on-line monitoring. The other main USN conditions are given in Table 35, and the ICP-OES operating conditions are listed in Table 36.

Table 35: Operating conditions for the USN

parameter	target Value	typical High Value	typical Low Value
desolvator temperature	170°C	171°C	168°C
condenser temperature	0°C	0.5°C	-0.2°C

Table 36: ICP operating parameters

Parameter (units)	value
generator frequency (MHz)	27.15
power RF (kW)	1.65*
plasma gas flow rate (L min^{-1})	20.0
auxiliary gas flow rate (L min^{-1})	0.8
aerosol carrier gas flow rate (L min^{-1})	0.5
Sample gas flow rate (L min^{-1})	0.125
injector tube diameter (mm)	1.8
read time (s)	44

** - the power was reduced slightly, with the aim of reducing the stress on the instrument, following the failure of the oscillator board in 2003, after continued full power operation.*

The ICP-OES was calibrated using 0-10 ppm EPA standard solutions (which correspond to 0-4.4 mg m^{-3} in the gas phase) in a range of gas matrixes produced from the calibration gases. Six gas compositions were used, comprising of 79% nitrogen, and 0-21% oxygen, with the remainder being carbon dioxide. Multi-variable linear regression analysis was used to correlate analyte emission signals with both concentration of metal and concentration of oxygen, and for each data point collected, the plant oxygen measurement was used to select the correct calibration statistics for the sample matrix at the point of measurement. For a few lines, the effect of carbon dioxide was insignificant, in which case simple linear regression was used to correlate count value to analyte concentration. On-line calibration checks were performed occasionally during experimental runs by nebulising a known standard during flue gas measurements, and were generally found to be quantified within the ± 20% demanded for CEM technologies, after a correction had been made for the signal due to metal in the flue gas at the point of calibration check.

Achieving reliable analytical measurements in the un-cleaned flue gas was very challenging. The un-cleaned gas provided an extremely difficult analytical matrix, with very high particulate loading, and very high and variable concentrations of a number of metals, along with trace concentrations of others. The heated sample line and analytical instrument was only designed for sampling of small particulates and gases, with particle sizes not over 10 μm, hence the use of the sampling train at the plant end of the line to remove larger particulates, and during long monitoring periods, problems were experienced with the deposition of large particles, leading to poor quantification.

Given the extreme conditions for analysis, and limited particulate sampling, the results are best considered as semi-quantitative indicators of volatile metal concentration in the flue gas (present as vapour or particles less than 10μm), with recognition that changing gas composition, limited sample deposition, and high plasma particulate loading will all have lowered analytical accuracy from its ideal optimum. Nevertheless, the data presented is unique, and illustrates a number of extremely interesting features observed in un-cleaned incinerator flue gas. The results of this unique experimentation are given in Chapter 5.

Chapter Four:

Thermodynamic Prediction of Equilibrium in a MSW Incinerator

The concept of thermodynamic prediction of equilibrium in MSW incineration was introduced in Chapter 2. A range of available computational packages are reviewed which may be used to predict the thermodynamic equilibrium condition of complex systems. Thermodynamic equilibrium calculations have been calculated using the FactSage™ programme, to predict the equilibrium behaviour of metals in a waste incinerator. Predictions were made for waste in the combustion chamber, and during gas cooling in the energy recovery system. A range of operational and input values were considered (e.g. chlorine concentration), in order to assess the sensitivity of the combustion system to changes in feed and operational conditions. The aim was to discover whether the known behaviour of waste incinerators could be rationalised through thermodynamic explanations, and further to examine whether temporal variations in metal concentrations could be attributed to thermodynamic and compositional changes in the waste combustion environment.

A number of "specific items" were identified in the waste stream whose behaviour it was thought may differ significantly from the overall equilibrium during the initial waste combustion stage. Attempts were made to calculate the equilibrium around such items on the burning bed, in order to assess how significant inhomogineity in the waste feed may be in influencing metal partitioning. Items considered included batteries, lead-containing PVC, and the glass from a cathode ray tube display screen. It was thought that data obtained on the equilibrium around such items may help to further rationalise observed partitioning behaviour which were not fully explained by bulk composition calculations.

The computational package used was FactSage™, one of the most comprehensive and versatile thermodynamic prediction systems available. It was particularly useful in this context as it is very good at the prediction of slags and melts, which can suppress volatility, and are therefore believed to be significant in determining the partitioning of metals in MSWI. The capabilities of this package are discussed in detail, following a short explanation of why this programme was chosen in preference to others which were available. Here it is appropriate to acknowledge the contribution to the project by Professor Bernard Argent, in the Engineering Materials Department of the University of Sheffield, who gave advice in the selection of appropriate modelling techniques, and the specific computational package, and used his copy of the FactSage™ software to produce the equilibrium calculations required.

4.1 Thermodynamic Equilibrium Prediction

The concept that reaction thermodynamics influences the extent and nature of reactions in chemistry has been in common usage for many years. The realisation that equilibrium products can be calculated for a system if the Gibbs energy is minimised is a powerful tool in predicting chemical reaction. It also allows reaction outcomes to be manipulated by changing the conditions (e.g. temperature or pressure) under which the

reaction is performed (i.e. Le Chatelier's principle). Such calculations can be performed for a simple reaction using a paper, pencil, and a calculator, provided that the experimental data (equilibrium constant and reaction Gibbs energies) are known (Atkins, 1994).

From this principle, it was recognised that thermodynamic predictions could provide a useful indicator to the behaviour of complex industrial processes (including combustion), where a large number of reactants and products were possible. Furthermore, a greater understanding of the thermodynamics could allow manipulation of the equilibrium products. However, the mathematical requirements for such calculations were far more complex than for a simple reaction, and therefore a computational method was required to calculate the results. Consequently a number of computer packages have been developed to calculate the equilibrium condition of such complex systems. Some of these programmes are general, and are applicable to numerous systems, and others are designed for more specific applications (Factsage, 2005, Infochem, 2003, Nenes et al., 1998).

Although there are a variety of user interfaces, the databases utilised overlap significantly, being effectively compilations of all thermodynamic data currently available (and relevant to the equilibrium being considered). Despite the variety of programmes, the thermodynamic approach remains the same; at its simplest the minimisation of the total Gibbs energy for the system under consideration. The computational problem remains in obtaining that energy minimum in a complex system. In part, this is achieved by the software packages themselves, but there is also considerable onus on the user to specify a problem to solve which makes the simplifications necessary in order to achieve a result, without introducing serious error through over-simplification, for example by failure to consider a possible set of reaction products (Argent, 2004).

The advances in computational thermodynamic equilibrium programmes have been significant in recent years. Increases in computing power have allowed much more complex systems to be modelled in reasonable time, and the sophistication of the thermodynamic packages has increased as the technology has become established, and the technique more common. Both the user computing packages (user interface, underlying computational methods, operating system for the software), and the thermodynamic information on which the models are based, have undergone significant improvement in recent years (Argent, 2004, Factsage, 2005, Powell and Holland, 2001).

There have been significant expansions to the underlying thermodynamic databases used in the calculations. Most significant for this work is the fact that slagging reactions, such as the formation of alkali metal melts ("glasses"), which may serve to trap heavy metals in vitrified materials, can now be considered. There have also been significant increases in the number of reactant and product species which may be considered, which means that the whole combustion system may be calculated as one equilibrium, whereas in the past, reactions for different metals would have to be considered separately, for computational reasons. Thus the treatment of metal-metal interactions has improved substantially, and the results from modern calculations should better reflect the equilibrium of the system as a whole, rather than some part of it (Argent, 2004, Factsage, 2005, Powell and Holland, 2001, Wu and Biswas, 1993).

Nevertheless, there remains a lack of thermodynamic data, leading to assumptions which may lower the accuracy of the model. Generally, these assumptions are interpolation of data for known compounds to provide general data for further compounds, for which measured values are not available. However as data availability increases (whether measured by experiment, or calculated mathematically), so does the ability to accurately estimate values for those where data is still unavailable. Thus the ability to predict the equilibrium for complex systems has improved significantly in recent years, and it is to be expected that improvement will continue in years to come, making thermodynamic calculations a sophisticated and powerful tool in predicting and explaining the behaviour of complex systems (Kemper, 2005, Argent, 2004, Powell and Holland, 2001).

4.2 Application of Thermodynamic Equilibrium Calculation to Municipal Solid Waste Incineration

Despite the great advances in thermodynamic equilibrium prediction tools, and the potential accuracy of the results obtained, a great deal of care must be exercised when applying such a technique to the combustion of municipal waste, as introduced in Chapter 2. The majority of the difficulties lie not in obtaining a good prediction of the thermodynamic equilibrium of the system, but in considering how far the assumptions of thermodynamic equilibrium are reasonable for such a system.

Firstly, in order that thermodynamic equilibrium is reached, it must be assumed that all the reactants are well mixed (homogeneous), and that reactions are able to reach equilibrium (i.e. the system is time-stable). Clearly, neither of these assumptions are strictly true for municipal waste combustion. Given the known inhomogeniety of the waste stream, it is likely that the assumption of good mixing is most significant, although kinetics may also be a factor (Delay, 1998). Thus it must immediately be acknowledged that a thermodynamic model will not give a full, quantitative prediction of the behaviour of waste during incineration, as the assumptions are significant, although such a model could still yield extremely useful information about how the system behaves.

Secondly, in order to obtain a good thermodynamic model of a system, it requires that the whole process is well characterised. Both the elemental input and the temperature at which equilibrium is obtained must be well known. Again, this is evidently a significant assumption for waste combustion, and considerable effort has to be made to ensure that the model inputs reflect the inputs to the incinerator. In some cases, where these values are known to change significantly with time, or their exact values are very poorly known, the best technique is to consider a range of values, and thus obtain a range of predictions for different conditions, and this has been done for some parameters in the waste combustion models.

Finally, it must be emphasised that thermodynamic models only predict evaporative transport routes for metals, and do not consider the effects of entrainment, which are significant in waste combustion (Belevi and Moench, 2000b, Linak and Wendt, 1993). Thus these three influences mean that the models produced in this work are not expected to be predictive and quantitative, but rather to see how observed data may be explained, and how changes to the waste input or combustion conditions may affect metal volatilisation. To this end, the models produced are extremely valuable, but it must be remembered that there are significant known errors associated with applying

the modelling technique to this particular system, and interpret the results accordingly (Argent, 2004).

4.3 Choice of Thermodynamic Equilibrium Package to model Municipal Solid Waste Incineration

As the popularity of the use of thermodynamic modelling packages has increased, the number of different software packages and data sets has increased. Rather than review a number of essentially similar programmes, this review concentrate on the one chosen for this work, and explain why it was selected. Three packages were considered in detail for calculating the equilibrium condition for waste combustion: NTData, THERMOCALC, and FactSage™. (Powell and Holland, 2001, Factsage, 2005).

NTData is an older thermodynamic equilibrium calculation package, which does not run under windows. Although the data obtained using this programme can be extremely detailed for well specified problems, the less convenient user interface meant that the programme was not considered appropriate for this work. Highly accurate models were not felt to be beneficial, given the variability in the waste feed and operating conditions, which could not be fully accounted for in a static model in any case (Argent, 2004), making an extremely sophisticated thermodynamic prediction rather meaningless.

ThermoCalc is a Windows® based thermodynamic equilibrium prediction programme. It shares many data sets with the NTData, but has an updated user interface. It is capable of giving highly detailed information on the equilibrium composition of complex reaction mixtures. However, the user interface is still relatively difficult to use, and it was considered that the value of more detailed information, at the expense of a more difficult calculation was questionable, given the limitations already described for applying conditions of thermodynamic equilibrium to waste combustion, and the inherent error introduced by the assumptions made (Powell and Holland, 2001, Argent, 2004).

The FactSage™ suite of programmes was chosen, for modelling MSW Incineration, as this was felt to be the most useful thermodynamic equilibrium prediction system available in-house for this problem. FactSage™ was developed by the University of Montreal, and is a windows based application designed for predicting the thermodynamic equilibrium in a variety of systems. It is a highly robust thermodynamic prediction tool, with a wide freedom to vary the input parameters, and so to examine "extreme" situations which may differ widely from generally assumed conditions. It was thought that this may be useful for developing "limiting cases" for thermodynamic behaviour within the burning bed for municipal waste combustion, where "non-standard" situations are frequently encountered. The programme is also very good at considering slagging reactions (aluminosilicate and alkali metal melts), which are believed to be significant in the trapping of metals in the bottom ash of incinerators. However, for the majority of calculations, only oxide slag melts could be considered, as adequate data were not available to consider more complex slag formation (e.g. for chloride and sulphate metal salts).

The ability to use the programme to calculate equilibrium for a wide range of input parameters requires that the problems solved are specified with care; otherwise unrealistic situations may be modelled, with the consequence of obtaining unrealistic

answers. Thus attention is required to obtaining good input data, and to using experience and discretion in determining which species should be considered (Factsage, 2005, Argent, 2004, Delay et al., 2001).

The FactSage™ application is based on two earlier programmes, FACT (Facility for the Analysis of Chemical Thermodynamics) and ChemSage©. It combines the powerful and comprehensive thermodynamic calculation capabilities of ChemSage© with the more convenient Windows® interface of FACT. The FACT programme was developed at the Ecole Polytechnique in Montreal, Canada, and the ChemSage programme by Dr Gunnar Eriksson, in Germany. The current FactSage Application has been developed by GTT Technologies (Chemsage, 2005, Factsage, 2005).

The package was used to calculate the minimal Gibbs energy for a multi-component phase equilibrium, using the EQUILIB programme. The input parameters were carefully chosen to reflect the typical composition and incineration conditions of MSW. The data for this was assembled from a large number of sources, and thus a range of values for most parameters was obtained, due to the variability of the waste stream. A single value was chosen from the range by excluding outliers, and taking an approximate mid-point of remaining values, with extra weighting being given to more "reliable" data sources, and the plant-specific experimental data.

Up to 40 different components (elements or compounds) can be specified as the input for the thermodynamic calculation and up to 1500 products can be considered in the most recent software version (Factsage, 2005). Priority was given to those elements with particular environmental, structural, or reactive properties. Along with toxic "heavy metals" and major "bulk elements" (such as Fe), alkali metals and alkali earth metals were included because of their tendency to participate in slag/melt formation, reducing volatility, and chlorine was included because of its tendency to enhance volatility of some metals. However, the improvements in the most recent version of this advanced computational package mean that the modelled situation was not generally limited by computational constraints, unlike previous similar calculations. In general, the elements not modelled were trace or ultra-trace metals with low reactivity and volatility, and these were only excluded if computational constraints required it.

Where necessary some product species were excluded from the specified problem. This included species which would not be expected in the given prediction conditions, or for which adequate data was not available for the modelled conditions. To assist in these decisions, the thermodynamic data sets in the programme include the temperatures over which a particular species is likely to form, so those which lie outside the available temperature range could be ignored. Although the programme provided as much information as possible about which species were likely to be significant in a given equilibrium, the good specification of the input parameters relied largely on the experience and expertise of those using the software. In addition, a post-calculation equilibrium activity calculation was performed, to ensure that no significant species were accidentally excluded from the initial part of the calculation. This calculation was used to check that no products predicted to have high activity ($>10^{-5}$) had been excluded from the main calculation, and amend the prediction if necessary (Argent, 2004). The results obtained were examined in the "results" and "figure" modules of the software, and could also be exported as data files for use in other programmes.

4.3.1 Solution Method

The thermodynamic solution desired was the lowest total Gibbs energy (G). For a particular set of elements, this was determined for a given temperature and pressure, by summing the product of the molar Gibbs energies (g) and the corresponding mole numbers (n) for all the compounds formed at equilibrium, and adding terms for the Gibbs energy of mixing.

The Gibbs energy (KJ mol^{-1}) of a single compound at any temperature is given by:

$$g = \left(\Delta H^{o} + \int_{298}^{T} Cp dT \right) - T\left(S^{o} + \int_{298}^{T} \frac{Cp}{T} dT \right) \quad (19)$$

Where: ΔH^{o} is the molar enthalpy of formation (KJ mol^{-1})

S^{o} is the absolute molar entropy (KJ K^{-1} mol^{-1})

and Cp is the constant pressure molar heat capacity (KJ K^{-1} mol^{-1})

The total Gibbs energy function (G) (KJ mol^{-1}) of the whole system, is given by the sum of these components, with two further terms to account for the Gibbs energy of mixing:

$$G = \sum_{i=1}^{m} n_i g_i + RT \sum_{j=1}^{a} n_j \ln(X_k P) + RT \sum_{k=1}^{b} n_k \ln(X_k) \quad (20)$$

Where: R is the gas constant (=8.31451 J K^{-1} mol^{-1})

and X is the mole fraction (dimensionless)

This equation applies to ideal solutions. In order to deal with real solutions, the mole fraction X_k of substance k is replaced with the activity, a_k, where the activity can be expressed in terms of the product of the mole fraction X_k, and the activity coefficient γ_k (ie $a_k = \gamma_k X_k$). However, for dilute solutions where information is limited, the activity constant is often assumed to equal one, and this assumption was made in most of the calculations for MSW incineration.

The thermodynamic solution will also obey the Gibbs Phase rule:

$$F = C - P + 2 \quad (21)$$

Where: F is the number of degrees of freedom (dimensionless)

C is the number of chemical components (dimensionless)

and P is the number of phases at equilibrium (dimensionless)

For vapours in equilibrium with one another, the method used for thermodynamic equilibrium prediction assumed scheil cooling. This was used for predicting the cooling behaviour of flue gases passing through the energy recovery system of the incinerator. In this method, equilibrium is calculated at a given temperature for all gaseous species, but it is assumed that any condensed species are removed from further equilibrium calculation. The temperature is then decreased, and another iteration is

performed, until the specified lowest temperature is reached. Predictions of metal volatility in the combustion chamber were used to provide the input parameters (elemental concentrations) for the gas cooling calculations.

4.3.2 Output Format

The thermodynamic calculation predicts the amount, and state, of all of the specified product compounds arising from the equilibrium of the input elements that were specified in the definition of the problem. The results could be expressed in a number of ways, including profiles of the activity of different products over a range of temperatures and percentages of a given element found in all the possible compounds predicted. These two formats were the ones most frequently used in this work.

4.4 Prediction of Thermodynamic Equilibrium for Municipal Waste

Using the computational package FactSage^{TM}, with the method described above, a series of calculations were performed to examine the thermodynamic equilibrium for the combustion of municipal waste. Various calculations were performed, for a range of possible waste and combustion scenarios, using the data given in section 4.4.1 – section 4.5, below.

The FactSage databases for gases and solid compounds were used. However, no database could be expected, or is available to give complete coverage of the slag forming potential of all the elemental components modelled (Ag, Al, As, Ba, C, Ca, Cd, Cl, Co, Cr, Cu, F, Fe, H, Hg, K, Li, Mg, Mn, Mo, N, Na, Ni, O, Pb, S, Sb, Si, Sn, Ti, Zn). The FactSage "slag ?" database was used excluding sulphides, sulphates, fluorides and chlorides. Oxides covered were Cu_2O, As_2O_3, ZnO, PbO, Cr_2O_3, CrO, Fe_2O_3, NiO, K_2O, Al_2O_3, CaO, Ti_2O_3, TiO_2, SiO_2, Na_2O, MnO, FeO, MgO. It must be recognised that this approach is not an approved use of the database as a very little is known about many of the potential interactions between the oxide components. The approach is used with the expectation that the behaviour of the major slag forming components Al_2O_3, CaO, FeO, Fe_2O_3 and SiO_2 should be reasonably covered with a less satisfactory coverage of the alkaline oxides. The availability of data for the slag-forming potential of trace heavy metals is even poorer, and for many of the calculations, such interactions could not be modelled, leading to higher volatilisation than seen in practice. For typical municipal waste only, attempts were made to overcome this limitation, as explained in section 4.4.1.

The total number of possible gaseous and solid compounds for the elements included in the calculations is far greater than can be used by the EQUILIBRIUM program of FactSage and use was made of a facility PREDOMINANT to identify the most important species to use in the final calculations.

For scheil cooling of the gas from 950° to 300°C formation of slag was not predicted but consideration was given to the possibility of a salt solution based on the carbonates, chlorides, fluorides, hydroxides, nitrates and sulphates of the alkali metals. In the absence of data on the most important trace elements calculations were undertaken for ideal solutions of antimony, cadmium and lead chlorides so as to obtain an impression of whether salt solutions were likely to be important.

4.4.1 Prediction of Equilibrium Products from Typical Municipal Waste

Due to its inherent inhomogeneity, and poor characterisation, an adequate description of "typical municipal waste" is extremely difficult, as explained in Chapter 2.

Nevertheless, it was important to consider how "typical" waste would be likely to behave under "typical" combustion conditions, so a series of calculations were performed at combustion temperatures, for a composition of waste which was considered to be typical, based on the best information available from numerous sources.

In the first set of calculations, the modelling parameters are exactly as given in section 4.4, but as indicated, this led to over-estimation of the volatilisation of some heavy metals, as their ability to dissolve in slag melts could not be properly modelled. Therefore, in a second series of calculations, the oxides BaO, Sb_2O_3, SnO_2, CdO and CoO were allowed to dissolve in the slag as ideal solutions. Again, this approximation is not an approved use of the database, as it fails to consider the enthalpy of interactions between the slag and these oxides, due to the lack of data. However, the low concentrations of the trace elements makes the absence of interaction information about the oxides of these elements less important, and so the calculation provides a "limiting case" situation for reduced heavy metal volatilisation, due to slag formation.

Input Parameters

The parameters chosen for the initial calculation, which was for the burning bed equilibrium of general municipal solid waste during incineration, are shown in Table 37. Water was specified separately from fuel hydrogen and oxygen, as water content of the fuel can have a significant effect on the thermodynamic equilibrium, of the reaction. These starting components account for 99.9% of the waste by mass. This is an excellent mass-balance closure, given that there will be some contribution from elements not listed, and that there is uncertainty associated with the figures given, due to the heterogeneous nature of the waste. The data is a complex summary of a variety of information from different sources, selected in order to give a good overall mass-balance, and includes data from our own experimentation.

Table 37: Input parameters for thermodynamic calculation of "typical municipal waste"

element	waste composition (ppm)	typical range (ppm)	comment
Ag	5		
Al	16000	6000 - 16000	
As	5		
Ba	300		
C	318000		total content
Ca	20000	10000-35000	very difficult to get a consistent estimate due to masking effect of Ca from lime injection
Cd	12		
Cl	9000	6000 - 14800	
Co	3		
Cr	200		
Cu	1000		very variable – large range of values
F	150		
Fe	25000	10000-50000	very variable source data
H	42000		H as fuel only
H_2O	300000	280000-320000	Not included in separate H or O values. Range from item to item probably significantly higher.
Hg	1		
K	3000	2000-5000	
Li	10		
Mg	3600	1000-4000	
Mn	300	300	
Mo	10	10	
N			from air, calculated to give correct flue gas composition
Na	5000	2000-7500	
Ni	100	100	
O	200000 from fuel	5-15% in bulk flue gases	figure calculated set to give 11 % O2 in flue gas (or other level as specified)
Pb	750	300-1000	
S	2000	1200-4000	
Sb	40		
Si	50000		probably an underestimate due to poor solubility of silicates in most analyses
Sn	250		
Ti	1600		
Zn	1500	500-3000	

Calculations were performed assuming a pressure of 1.0 atmosphere (which is a reasonable assumption, although in practice the furnace is kept under a very slight negative pressure), and a normal oxygen level of 11%, which is typical for the bulk properties of a municipal incinerator, although levels on the burning bed may be significantly lower, and this is considered in section 4.4.2. It was very difficult to specify an equilibrium temperature, as the temperature profile changes along the bed, and the bulk temperature may be significantly below the localised high temperatures. Thus the thermodynamic equilibrium was calculated for a range of temperatures between 700°C and 1300°C, corresponding to the widest range of the temperatures anticipated on the plant (Yang et al., 2002).

In terms of correlation to metal partitioning in a MSWI, it was assumed that any metal species present at equilibrium as solid or liquid would be found in the bottom ash, and that any species present as gases would be transported in the flue gas, and captured in the APC device, as it is known that essentially all heavy metals [with the possible exception of mercury] are effectively captured. Thus a two-part partitioning model was established. Scheil cooling calculations (introduced in section 4.3.1) were used to predict the temperatures at which metals would condense from the flue gas, and the species which would be likely to form.

4.4.2 Variable Sensitivity Study

Given the known heterogeneity of the waste stream, it was appreciated that the composition of waste burning at a particular time, or in a particular part of the furnace, could differ significantly from the "typical composition" specified above (Reimann, 1989, Delay et al., 2001). This is indicated in Table 37 by the typical range of concentrations quoted for some elements.

Further calculations were therefore conducted for "bulk municipal waste", considering high and low values for some of these waste input parameters, in order that the sensitivity of the equilibrium position to changes in composition could be assessed. From previous work, it was thought that as well as temperature and oxygen, moisture [water] content, chlorine, sulphur and alkali (Na + K) could have an important influence on metal partitioning (Belevi and Moench, 2000a, Delay et al., 2001, Abbas et al., 1996, Zhao et al., 2004). In some cases, two factors were altered together (e.g. chlorine and alkali content), as it was anticipated that a change in one could have an effect on the influence of another. Table 38 indicates the input parameters selected for sensitivity study. The "high" and "low" values used for this study were usually twice and half the "typical" value for a particular input, as this seemed normally to represent the range of values expected for each parameter. Unless otherwise stated, all other variables took the "typical values" stated in Table 37, while the variable being studied was altered. Although the value of considering enhanced dissolution was investigated for typical municipal waste, the general slag solution model (excluding Ba, Cd, Co, Sb and Sn) was used for the variability sensitivity studies, to reduced calculation complexity, and minimise the potential error introduced by the modelling technique.

Table 38: The input parameters selected for sensitivity studies, and the ranges examined

sensitivity study parameters	typical composition (ppm)	low value used	high value used	purpose / comments
Cl	9000	4500	18000	to see effect of high/low Cl
H_2O	300000	150000	600000	to see effect of high/low water
O	11%	5%	21%	Only low value used, to represent oxygen starvation during intense combustion. High oxygen not normally encountered (would correspond to poor combustion).
O and H_2O				High water and high oxygen used to represent poor combustion, low oxygen and water to represent intense combustion, to see combined effect from multiple factors
Na	5000	2500	10000	to see if alkali has effect on heavy metal transport, due to its known interactions with Cl
Na and Cl				high Cl and low Na, and low Cl and high Na used to further examine relationship between heavy metal transport by Cl and effect of alkali on this

4.4.3 Results: "Typical" Municipal Waste Equilibrium

Waste Combustion Equilibrium

The results of the thermodynamic equilibrium prediction of the combustion products from "typical" municipal waste, combusted at a range of expected temperatures is shown in Table 39 [Page 126] for all key elements. The table indicates the distribution between gaseous, solid, and slag phases, and shows the key species identified for each. Compounds predicted down to at least 0.005% are shown, with the most significant species predicted at lower concentration being shown, where none are predicted in significant quantity. In this calculation, dissolution in the slag was not allowed for the trace metals Ba, Cd, Co, Sb and Sn, for which mixing data was not available.

These results clearly differentiate the elements into volatile, semi-volatile, and non-volatile, broadly as expected under the incineration conditions specified. For example, oxygen, mercury and chlorine are completely volatilised, Aluminium and silicon are not volatilised significantly at all, and sodium, tin and lead are volatilised to some extent. For the semi-volatile metals, volatilisation is almost always seen to be higher at higher temperature. Slag formation is generally seen to be increased at higher temperature, at the expense of less pure solids remaining. However, for some volatile metals, such as potassium, slag formation reduces at the highest temperature, as gaseous products become the most significant. Chlorides are seen to be significant in volatilisation, as are oxides and native metals for some elements. For the more volatile metals such as lead, chlorides tend to be more important to volatilisation at lower temperatures, with oxides and native metals dominating at higher temperatures. For only slightly volatile metals such as cobalt or copper, the chlorides remain the significant volatile species throughout the temperature range considered.

Table 40 [Page 127] shows how the equilibrium combustion products change for the elements Ba, Sb, Sn, Cd, and Co when approximations are made to allow the dissolution of the oxides of these metals in the slag melt. For Cd, Co, and Sb, this significantly reduces the volatility of the metals, as slag formation becomes more important. For all the others, the importance of pure species is reduced, as more slag formation occurs, even if this does not affect volatilisation significantly. However, for barium, the effect is small, as dissolution in the slag remains low. Although the

equilibrium distribution of other metals remains broadly the same, it should be noticed that the change in modelling conditions causes perturbation to the equilibrium position, so the exact mass distribution values for other elements changes slightly (please note that the lowest temperature shown in this calculation is increased to 750°C, due to the very low slag formation at lower temperatures).

Figure 43 - Figure 45 illustrate how the composition of the equilibrium products from incineration (second calculation) change with temperature. While many of the compounds remain in almost constant amount throughout the temperature range (e.g. carbon dioxide, oxygen and water content), others increase (e.g. Zn) or decrease (e.g. $ZnCl_2$) with changing temperature. It is quite clear that slag formation is minimal at low temperatures, with the amount of slag significantly increasing over about 825°C. For the volatile metals Cd and Pb, the amount dissolved in the slag decreases with temperature, as volatilisation increases.

Table 39: Predicted distribution of elements among major species: percentage of total amount (wt %) at different temperatures, and key species

element	products predicted	700°C	key species	850°C	key species	950°C	key species	1300°C	key species
Al	Al in slag	0.00		34.22	Al2O3	42.90	Al2O3	100.00	Al2O3
	pure solid	100.00	CaAl2Si2O8, NaAlSi3O8, KAlSi2O6, Mn3Al2Si3O12	65.77	CaAl2Si2O8	57.10	CaAl2Si2O8, KAlSi2O6	0.00	
As	As in slag	0.00		100.00		100.00	As2O3	99.98	
	pure solid	100.00	Ca3(AsO4)2	0.00		0.00		0.00	
Ba	gas	0.00		0.00	BaCl2	0.01		0.28	BaCl2, Ba(OH)2, BaO
	pure solid	100.00	BaSO4	100.00	BaSO4	99.99	BaCrO4	99.72	(BaO)(SiO2)
C	gas	100.00	CO2, CO	100.00	CO2, CO	100.00	CO2, CO	100.00	CO2, CO
Ca	Ca in slag	0.00		16.98	CaO	35.05	CaO	99.98	CaO
	pure solid	100.00	CaAl2Si2O8, MgOCaOSi2O4, Ca3Fe2Si3O12, CaSO4, CaSiTiO5, (CaO)(MoO3)	83.02	CaAl2Si2O8, MgOCaOSi2O4, Ca3Fe2Si3O12, CaSiTiO5	64.95	CaAl2Si2O8, MgOCaOSi2O4, CaSiTiO5, Ca3Fe2Si3O12	0.02	(CaO)(MoO3)
Cd	gas	2.87	CdO, Cd, (CdOH)	100.00	Cd, CdO (CdOH)	100.00	Cd, CdO (CdOH)	100.00	Cd, CdO (CdOH)
	pure solid	97.13	(CdO)(SiO2)	0.00		0.00		0.00	
Cl	gas	100.00	HCl, PbCl2, ZnCl2, LiCl, NaCl, Cl2, KCl, Cl, (CuCl)3	100.00	HCl, NaCl, PbCl2, ZnCl2, CuCl, LiCl, KCl, Cl	100.00	HCl, CuCl, KCl, NaCl, ZnCl2, PbCl2, Cl, LiCl	100.00	HCl, KCl, NaCl, Cl, CuCl, LiCl, ZnCl2, ClO
Co	gas	0.22	CoCl2, CoCl3	2.02	CoCl2, CoCl3	6.52	CoCl2, CoCl3	48.29	CoCl2, CoCl, Co
	pure solid	99.78	(CoO)(Cr2O3)	97.98	(CoO)(Cr2O3)	93.48	(CoO)(Cr2O3)	51.71	(CoO)(Cr2O3)
Cr	gas	0.00	CrO2	0.00		0.00		0.41	CrO2
	Cr in slag	0.00		0.00	Cr2O3	0.11	Cr2O3,CrO	35.33	Cr2O3, CrO
	pure solid	100.00	(MgO)(Cr2O3), (CoO)(Cr2O3)	100.00	(MgO)(Cr2O3), (CoO)(Cr2O3)	99.89	BaCrO4, (MgO)(Cr2O3), (CoO)(Cr2O3)	64.26	(MgO)(Cr2O3), (CoO)(Cr2O3)
Cu	gas	1.96	(CuCl)3, CuCl, CuF	18.33	CuCl, Cu2O, (CuCl)3, CuF	71.42	CuCl, (CuCl3), Cu, CuF,	73.09	CuCl, Cu, CuO, CuF
	Cu in slag	0.00		5.07		28.58	Cu2O	26.91	Cu2O
	pure solid	98.04	(CuO)(Fe2O3)(s	76.59	(CuO)(Fe2O3)(s	0.00		0.00	
F	gas	100.00	HF, OAlF2, LiF	100.00	HF, OAlF2, LiF, NaF, KF	100.00	HF, OAlF2, LiF, NaF, KF	100.00	HF, KF, OAlF2, NaF
Fe	gas	0.00	FeCl2	0.00	FeCl2	0.00	FeCl2	0.02	Fe(OH)2, FeCl2, FeO
	Fe in slag	0.00		0.00		0.06	Fe2O3	25.44	Fe2O3
	pure solid	100.00	Fe2O3, Ca3Fe2Si3O12, (CuO)(Fe2O3), (NiO)(Fe2O3)	100.00	Fe2O3, Ca3Fe2Si3O12, (CuO)(Fe2O3) (NiO)(Fe2O3)	99.94	Fe2O3, Ca3Fe2Si3O12, (NiO)(Fe2O3)	74.54	Fe2O3
H	gas	100.00	H20, HCl, HF	100.00	H20, HCl, HF	100.00	H20, HCl, HF	100.00	H20, HCl, HF, H2
Hg	gas	100.00	Hg, HgCl2, HgCl	100.00	Hg, HgCl2	100.00	Hg, HgCl2	100.00	Hg
K	gas	0.32	KCl	1.83	KCl	8.20	KCl, KOH, (KCl)2, KF	76.29	KCl, KOH, KF
	K in slag	0.00		98.17	K2O	78.19	K2O	23.71	K2O
	pure solid	99.68	KAlSi2O6	0.00		13.60	KAlSi2O6	0.00	
Li	gas	100.00	LiCl, (LiCl)2, LiOH, LiF	100.00	LiCl, LiOH, (LiCl)2, LiF	100.00	(LiCl, LiOH, LiF,	100.00	LiCl, LiOH, LiF
Mg	gas	0.00		0.00	MgCl2	0.00		0.00	Mg(OH)2
	Mg in slag	0.00		5.39	MgO	15.90	MgO	99.18	MgO
	pure solid	100.00	MgOCaOSi2O4, (MgO)(Cr2O3)	94.61	MgOCaOSi2O4, (MgO)(Cr2O3)	84.10	MgOCaOSi2O4	0.82	(MgO)(Cr2O3)
Mn	gas	0.03		0.07	MnCl2	0.03	MnCl2	0.01	MnCl2
	Mn in slag	0.00		99.93	MnO	99.97	MnO	99.99	MnO
	pure solid	99.97	Mn3Al2Si3O12	0.00		0.00		0.00	
N	gas	100.00	N2, NO	100.00	N2, NO	100.00	N2, NO	100.00	N2, NO
Na	gas	0.29	NaCl, (NaCl)2	2.81	NaCl, (NaCl)2, NaOH	2.71	NaCl, NaOH, (NaCl)2, NaF	7.80	NaCl, NaOH, Na, NaF,
	Na in slag	0.00		97.19	Na2O	97.29	Na2O	92.20	Na2O
	pure solid	99.71	NaAlSi3O8	0.00		0.00		0.00	
Ni	gas	0.02	NiCl2, Ni(OH)2	0.16	NiCl2, Ni(OH)2	0.41	NiCl2, Ni(OH)2, NiCl	1.24	NiCl2, Ni(OH)2, NiCl
	Ni in slag	0.00		0.50	NiO	6.16	NiO	98.76	NiO
	pure solid	99.98	(NiO)(Fe2O3)	99.35	(NiO)(Fe2O3)	93.44	(NiO)(Fe2O3)	0.00	
O	gas	99.49	O2, CO2, H2O, NO	99.50		99.51	O2, CO2, H2O, NO, SO2	99.51	O2, CO2, H2O, NO
	O in slag	0.00		0.21	SiO2, Na2O, CaO, K2O, MgO	0.25	SiO2, Al2O3, CaO, Na2O, K2O, Ti2O	0.44	SiO2, Al2O3, CaO, MgO, Na2O, FeO, Ti2O
	pure solid	0.51	NaAlSi3O8, CaAl2Si2O8, MgOCaOSi2O4	0.28	CaAl2Si2O8, MgOCaOSi2O4	0.24	CaAl2Si2O8, MgOCaOSi2O4	0.04	Fe2O3, (BaO)(SiO2)
Pb	gas	100.00	PbCl2, PbO, PbCl	91.86	PbCl2, PbO, PbCl, Pb	84.83	PbO, PbCl2, PbCl, Pb	99.12	PbO, PbCl, Pb, PbCl2,
	Pb in slag	0.00		8.14	PbO	15.17	PbO	0.88	PbO
S	gas	1.52	SO2, SO3	96.50	SO2, SO3	100.00	SO2, SO3, SO	100.00	SO2, SO3, SO
	pure solid	98.48	CaS04, BaSO4	3.50	BaSO4	0.00		0.00	
Sb	gas	0.14	SbCl3, (SbO2H2)	1.23	(SbO2H2), SbCl3, SbOH	8.50	(SbO2H2), SbCl3, SbOH	100.00	(SbO2H2), Sb, SbOH
	pure solid	99.86	SbO2	98.77	SbO2	91.50		0.00	
Si	Si in slag	0.00		56.85	SiO2	64.15	SiO2	99.88	SiO2
	pure solid	100.00	NaAlSi3O8, CaAl2Si2O8, MgOCaOSi2O4, SiO2, KAlSi2O6, Ca3Fe2Si3O12, CaSiTiO5, Zn2SiO4	43.15	CaAl2Si2O8, MgOCaOSi2O4, Ca3Fe2Si3O12, CaSiTiO5, SiO2, Zn2SiO4	35.85	CaAl2Si2O8, MgOCaOSi2O4, CaSiTiO5, KAlSi2O6, Ca3Fe2Si3O12, Zn2SiO4	0.12	(BaO)(SiO2)
Sn	gas	0.00		0.00		0.00	SnO, (SnO2H2), SnCl2	100.00	SnO, (SnO2H2), SnCl2
	pure solid	100.00	SnO2	100.00	SnO2	100.00	SnO2	0.00	
Ti	Ti in slag	0.00		9.67	TiO2	37.36	TiO2	100.00	TiO2, Ti2O3
	pure solid	100.00	CaSiTiO5	90.33	CaSiTiO5	62.64	CaSiTiO5	0.00	
Zn	gas	5.15	ZnCl2	8.55	ZnCl2	10.82	ZnCl2, Zn	10.06	Zn, ZnCl2
	Zn in slag	0.00		5.08	ZnO	41.30	ZnO	89.94	ZnO
	pure solid	94.85	Zn2SiO4	86.37	Zn2SiO4	47.88	Zn2SiO4	0.00	

Table 40: Predicted distribution of elements among major species: percentage of total amount (wt %) at different temperatures, allowing enhanced slag dissolution

element	products predicted	750°C	key species	850°C	key species	950°C	key species	1300°C	key species
Al	Al in slag	0.48	Al2O3	34.27	Al2O3	42.98	Al2O3	100.00	Al2O3
	pure solid	99.51	CaAl2Si2O8, NaAlSi3O8, KAlSi2O6, Mn3Al2Si3O12	65.73	CaAl2Si2O8	57.02	CaAl2Si2O8, KAlSi2O6	0.00	
As	gas	0.00	AsF3	0.00	AsF3	0.00	AsF3	0.02	AsN, As
	As in slag	1.43	As2O3	100.00	As2O3	100.00	As2O3	99.98	As2O3
	pure solid	98.57	Ca3(AsO4)2	0.00		0.00		0.00	
Ba	gas	0.00	BaCl2	0.00	BaCl2	0.01	BaCl2	0.28	BaCl2, Ba(OH)2
	Ba in slag	0.00	BaO	0.00	BaO	0.01	BaO	1.26	BaO
	pure solid	100.00	BaSO4	100.00	BaSO4	99.98	BaCrO4	98.46	(BaO)(SiO2)
C	gas	100.00	CO2	100.00	CO2	100.00	CO2	100.00	CO2, CO
Ca	Ca in slag	0.04	CaO	17.02	CaO	35.18	CaO	99.98	CaO
	pure solid	99.96	CaAl2Si2O8, MgOCaOSi2O4, Ca3Fe2Si3O12, CaSO4, CaSiTiO5, (CaO)(MoO3), Ca3(AsO4)2	82.98	CaAl2Si2O8, MgOCaOSi2O4, Ca3Fe2Si3O12, CaSiTiO5, (CaO)(MoO3)	64.82	CaAl2Si2O8, MgOCaOSi2O4, CaSiTiO5, Ca3Fe2Si3O12, (CaO)(MoO3)	0.02	(CaO)(MoO3)
Cd	gas	0.78	CdO, Cd	0.45	CdO, Cd	6.55	Cd, CdO	98.49	Cd, CdO, CdOH
	Cd in slag	99.22	CdO	99.55	CdO	93.45	CdO	1.52	CdO
Cl	gas	100.00	HCl, PbCl2, ZnCl2, NaCl, LiCl, KCl, CuCl, Cl, Cl2, (CuCl)3, AgCl, HOCl, ClO, (LiCl)2, MnCl2, (NaCl)2	100.00	HCl, NaCl, PbCl2, ZnCl2, CuCl, LiCl, KCl, (CuCl)3, Cl2, AgCl, PbCl, HOCl, ClO, (NaCl)2, MnCl2, NiCl2	100.00	HCl, CuCl, KCl, NaCl, ZnCl2, PbCl2, Cl, LiCl, (CuCl)3, Cl2, PbCl, AgCl, ClO, HOCl, NiCl2, MnCl2	100.00	HCl, KCl, NaCl, Cl, CuCl, LiCl, ZnCl2, ClO, FeCl2, AgCl, PbCl, HOCl, BaCl2, Cl2, NiCl2
Co	gas	0.09	CoCl2	0.00	CoCl2	0.01	CoCl2	0.01	CoCl2
	Co in slag	99.91	CoO	100.00	CoO	99.99	CoO	99.99	CoO
Cr	gas	0.00	CrO2	0.00	CrO2	0.00	CrO2	0.41	CrO2
	Cr in slag	0.00	Cr2O3	0.00	Cr2O3	0.11	Cr2O3	35.39	Cr2O3, CrO
	pure solid	100.00	(MgO)(Cr2O3)	100.00	(MgO)(Cr2O3)	99.89	BaCrO4, (MgO)(Cr2O3)	64.20	(MgO)(Cr2O3)
Cu	gas	3.93	CuCl, (CuCl)3	18.34	CuCl, (CuCl)3	71.31	CuCl, (CuCl)3, Cu, CuF	73.08	CuCl, Cu, CuO, CuF
	Cu in slag	0.00	Cu2O	5.10	Cu2O	28.69	Cu2O	26.92	Cu2O
	pure solid	96.07	(CuO)(Fe2O3)	76.56	(CuO)(Fe2O3)	0.00		0.00	
F	gas	100.00	HF, OAlF2, LiF	100.00	HF, OAlF2, LiF, NaF	100.00	HF, OAlF2, LiF, NaF, KF, CuF	100.00	HF, KF, OAlF2, NaF, LiF, CuF
Fe	gas	0.00	FeCl2	0.00	FeCl2	0.00	FeCl2	0.02	Fe(OH)2, FeCl2
	Fe in slag	0.00	FeO	0.00	FeO	0.06	FeO, Fe2O3	25.46	FeO, Fe2O3
	pure solid	100.00	Fe2O3, Ca3Fe2Si3O12, (CuO)(Fe2O3), (NiO)(Fe2O3)	100.00	Fe2O3, Ca3Fe2Si3O12, (CuO)(Fe2O3), (NiO)(Fe2O3)	99.94	Fe2O3, Ca3Fe2Si3O12, (NiO)(Fe2O3)	74.52	Fe2O3
H	gas	100.00	H2O, HCl, HF	100.00	H2O, HCl, HF, OH	100.00	H2O, HCl, HF, OH	100.00	H2O, HCl, OH, HF, H2
Hg	*gas*	*100.00*	*Hg, HgCl2*	*100.00*	*Hg, HgCl2*	*100.00*	*Hg, HgCl2*	*100.00*	*Hg*
K	gas	0.68	KCl	1.82	KCl	8.22	KCl, KOH, (KCl)2	76.29	KCl, KOH, KF, K
	K in slag	4.32	K2O	98.18	K2O	78.13	K2O	23.71	K2O
	pure solid	95.00	KAlSi2O6	0.00		13.65	KAlSi2O6	0.00	KAlSi2O6
Li	gas	100.00	LiCl, (LiCl)2, LiOH, LiF	100.00	LiCl, LiOH, (LiCl)2, LiF	100.00	LiCl, LiOH, LiF, (LiCl)2	100.00	LiCl, LiOH, LiF, LiO
Mg	Mg in slag	0.00	MgO	5.41	MgO	15.99	MgO	99.17	MgO
	pure solid	100.00	(MgO)(Cr2O3)	94.60	MgOCaOSi2O4, (MgO)(Cr2O3)	84.01	MgOCaOSi2O4, (MgO)(Cr2O3)	0.83	(MgO)(Cr2O3)
Mn	gas	0.05	MnCl2	0.07	MnCl2	0.03	MnCl2	0.01	MnCl2
	Mn in slag	0.05	MnO	99.93	MnO	99.97	MnO	99.99	MnO
	pure solid	99.90	Mn3Al2Si3O12	0.00		0.00		0.00	
Mo	pure solid	100.00	(CaO)(MoO3)	100.00	(CaO)(MoO3)	100.00	(CaO)(MoO3)	100.00	(CaO)(MoO3)
N	gas	100.00	N2, NO	100.00	N2, NO	100.00	N2, NO	100.00	N2, NO
Na	gas	0.67	NaCl, (NaCl)2	2.786	NaCl, (NaCl)2	2.69	NaCl, NaOH	7.804	NaCl, NaOH, Na, NaF
	Na in slag	1.02	Na2O	97.21	Na2O	97.31	Na2O	92.20	Na2O
	pure solid	98.31	NaAlSi3O8	0.00		0.00		0.00	
Ni	gas	0.05	NiCl2	0.16	NiCl2	0.41	NiCl2, Ni(OH)2	1.240	Ni(OH)2, NiCl2, NiCl
	Ni in slag	0.00	NiO	0.50	NiO	6.22	NiO	98.76	NiO
	pure solid	99.95	(NiO)(Fe2O3)	99.34	(NiO)(Fe2O3)	93.38	(NiO)(Fe2O3)	0.00	
O	gas	99.49	O2, CO2, H2O, NO	99.50	O2, CO2, H2O, NO, SO2, SO3	99.51	O2, CO2, H2O, NO, SO2, SO3	99.51	O2, CO2, H2O, NO, OH, SO2
	O in slag	0.00	SiO2	0.21	SiO2, Al2O3, Na2O, CaO, K2O	0.25	SiO2, Al2O3, CaO, Na2O, K2O, TiO2, MgO	0.44	SiO2, Al2O3, CaO, MgO, Na2O, FeO, TiO2
	pure solid	0.50	NaAlSi3O8, CaAl2Si2O8, MgOCaOSi2O4, Fe2O3, Ca3Fe2Si3O12, KAlSi2O6, SiO2, CaSO4, CaSiTiO5	0.28	CaAl2Si2O8, MgOCaOSi2O4, Fe2O3, Ca3Fe2Si3O12, CaSiTiO5, (CuO)(Fe2O3), Zn2SiO4	0.24	CaAl2Si2O8, MgOCaOSi2O4, Fe2O3, CaSiTiO5, KAlSI2O6, Ca3Fe2Si3O12, Zn2SiO4	0.04	Fe2O3, (BaO)(SiO2), (MgO)(Cr2O3), (CaO)(MoO3)
Pb	gas	*99.99*	*PbCl2, PbO, PbCl*	*91.82*	*PbCl2, PbO, PbCl*	*84.77*	*PbO, PbCl2, PbCl, Pb*	*99.12*	*PbO, PbCl, Pb, PbCl2,*
	Pb in slag	0.01	PbO	8.184	PbO	15.23	PbO	0.88	PbO
S	gas	12.01	SO2, SO3	96.50	SO2, SO3	100.00	SO2, SO3	100.00	SO2, SO3
	pure solid	87.99	SiS2, CaSO4, BaSO4	3.503	BaSO4	0.00		0.00	
Sb	gas	0.23	SbCl3, (SbO2H2)	0.21	(SbO2H2), SbCl3	0.56	(SbO2H2), SbCl3	10.32	(SbO2H2), Sb, (SbOH)
	Sb in slag	8.145	Sb2O3	99.79	Sb2O3	99.44	Sb2O3	89.68	Sb2O3
	pure solid	91.62	SbO2	0.00		0.00		0.00	
Si	Si in slag	1.14	SiO2	56.96	SiO2	64.21	SiO2	99.88	SiO2
	pure solid	98.86	NaAlSi3O8, CaAl2Si2O8, MgOCaOSi2O4, SiO2, KAlSi2O6, Ca3Fe2Si3O12, CaSiTiO5, Zn2SiO4	43.04	CaAl2Si2O8, MgOCaOSi2O4, Ca3Fe2Si3O12, CaSiTiO5, Zn2SiO4, SiO2	35.79	CaAl2Si2O8, MgOCaOSi2O4, KAlSi2O6, CaSiTiO5, Ca3Fe2Si3O12, Zn2SiO4	0.12	(BaO)(SiO2)
Sn	gas	0.00	SnCl2, (SnO2H2), SnCl4	0.00	(SnO2H2), SnCl2	0.00	SnO	0.19	SnO
	Sn in slag	100.00	SnO2	100.00	SnO2	100.00	SnO2	99.81	SnO2
Ti	Ti in slag	0.03	TiO2	9.70	TiO2	37.56	TiO2	100.00	TiO2, Ti2O3
	pure solid	99.97	CaSiTiO5	90.30	CaSiTiO5	62.44	CaSiTiO5	0.00	
Zn	gas	6.31	ZnCl2	8.56	ZnCl2	10.84	ZnCl2	10.05	Zn, ZnCl2
	Zn in slag	0.00	ZnO	5.11	ZnO	41.68	ZnO	89.95	ZnO
	pure solid	93.69	Zn2SiO4	86.34	Zn2SiO4	47.49	Zn2SiO4	0.00	

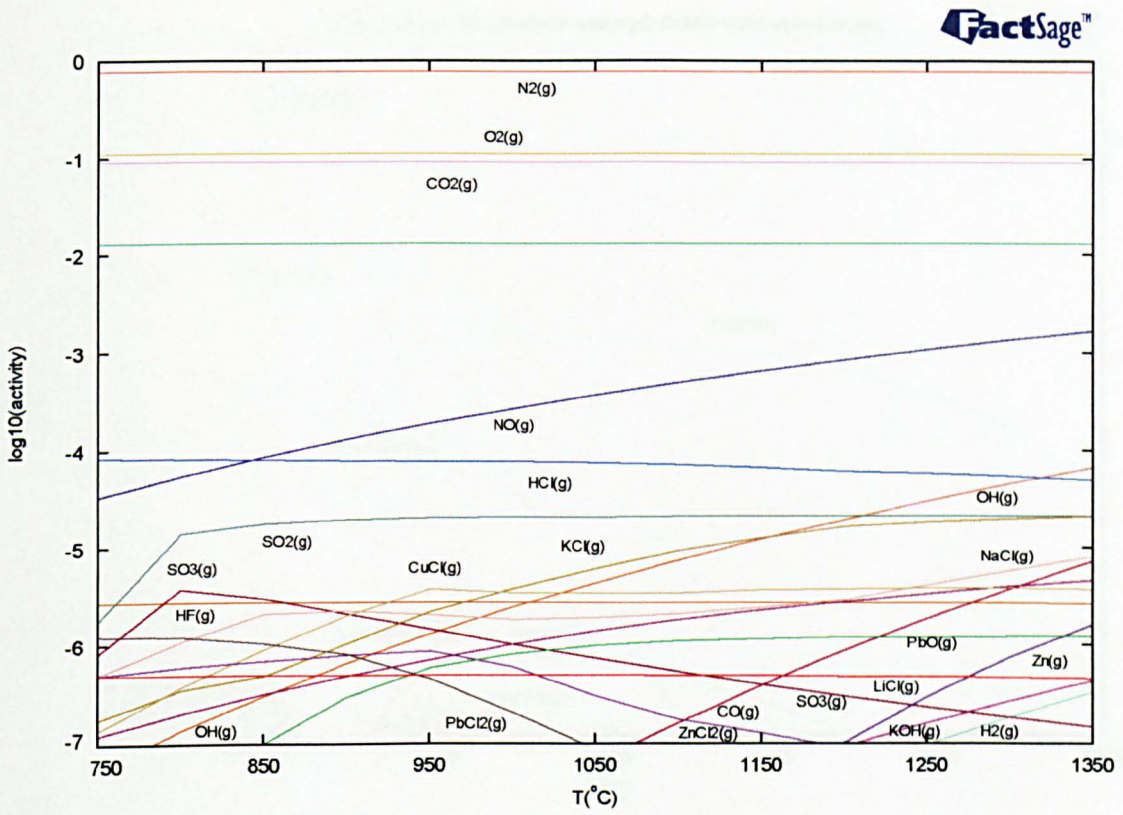


Figure 43: Principal gaseous compounds from "normal" MSW combustion over a range of temperatures

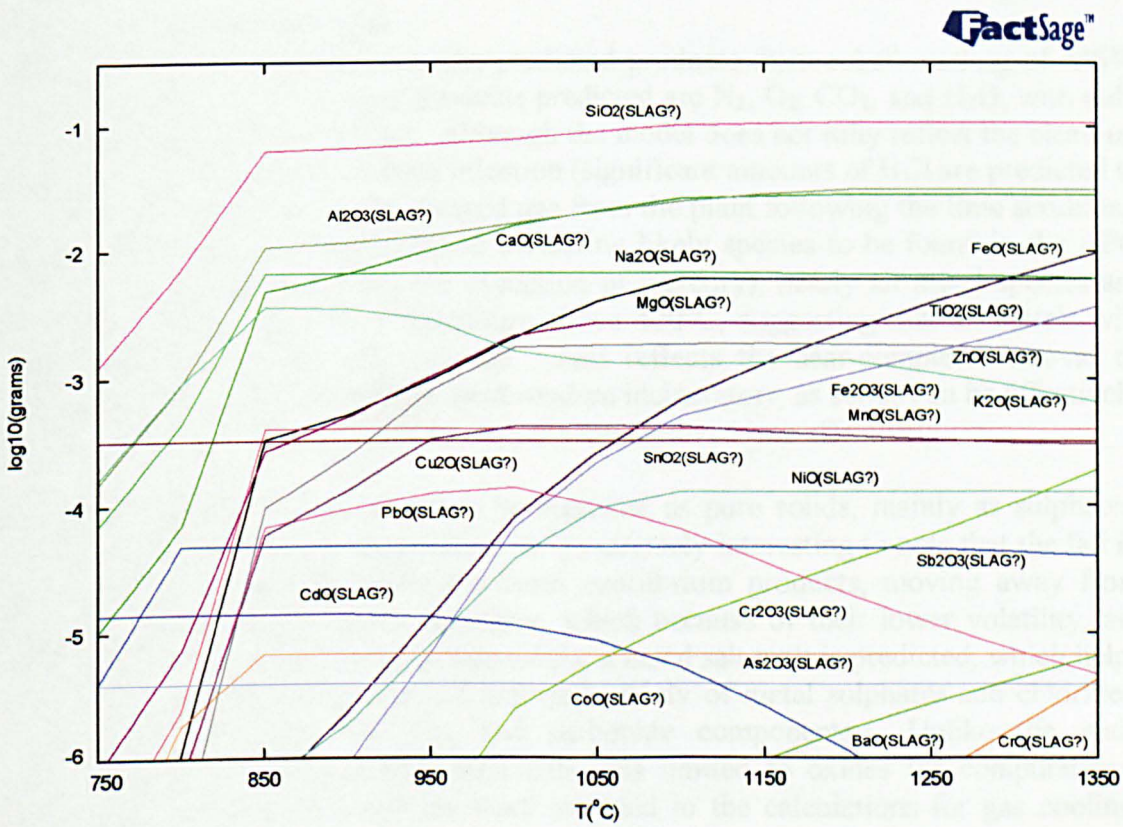


Figure 44: Principal slag components from "normal" MSW combustion over a range of temperatures

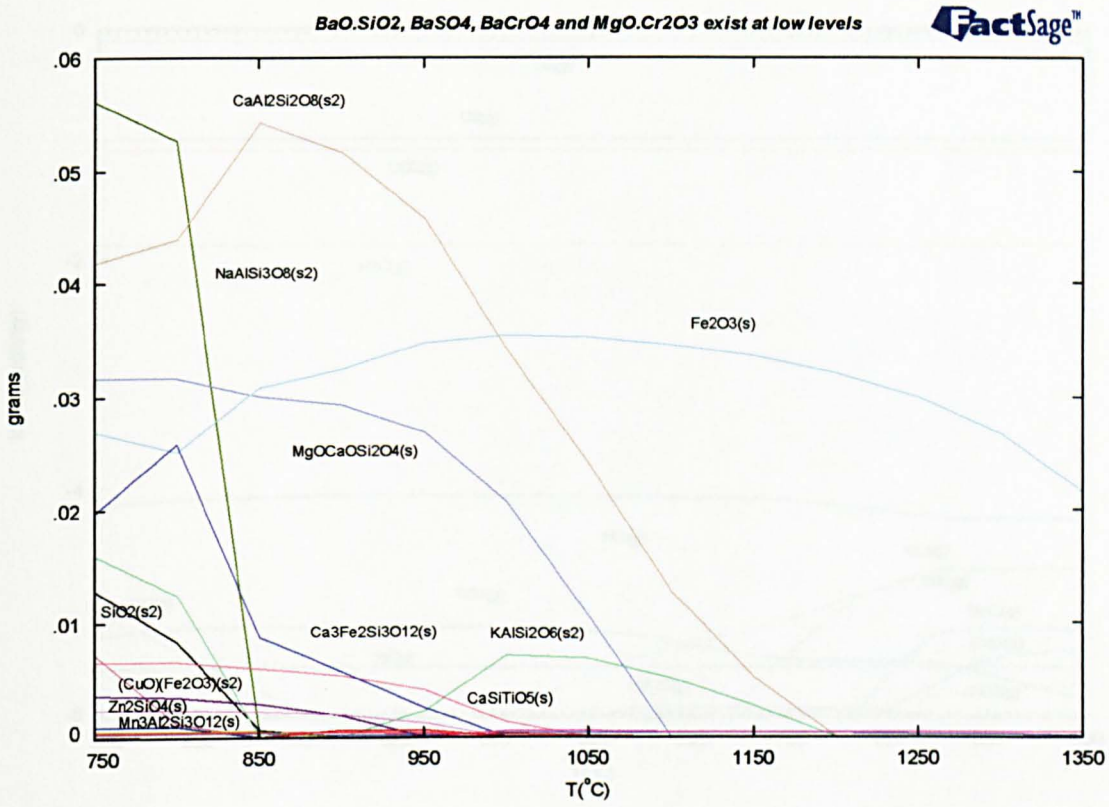


Figure 45: Principal pure solid species from "normal" MSW combustion over a range of temperatures

Waste Cooling Equilibrium

Figure 46 - Figure 48 illustrate the predicted products from scheil cooling of MSW incineration gases. The major products predicted are N_2, O_2, CO_2, and H_2O, with only small amounts of other species. Although the model does not fully reflect the clean-up achieved by the plant due to lime injection (significant amounts of HCl are predicted to remain but are not seen in the cleaned gas from the plant following the lime scrubbing stage), the model is most helpful in indicating likely species to be found in the APC residue. It is seen that (with the exception of mercury), nearly all metal species are predicted to condense at a temperature above 400°C, suggesting that all metals will have condensed before gas clean-up. This reflects the near-complete removal of metals from flue gas observed in most modern incinerators, as solids can be effectively removed during clean-up, whereas vapours are removed less effectively.

Numerous species are predicted to be removed as pure solids, mainly as sulphates, chlorides, hydroxides and carbonates. It is extremely interesting to note that the fall in temperature significantly alters the main equilibrium products, moving away from chloride species, and towards sulphates, which because of their lower volatility, aid condensation. In addition to the pure solids, a fused salt melt is predicted, which helps to remove metallic gases, and is comprised mainly of metal sulphates and chlorides, with some hydroxide, fluoride, and carbonate components. Unlike the main combustion calculations, where melt data was limited to oxides for computational reasons, all melt-forming species were included in the calculations for gas cooling, where data was available.

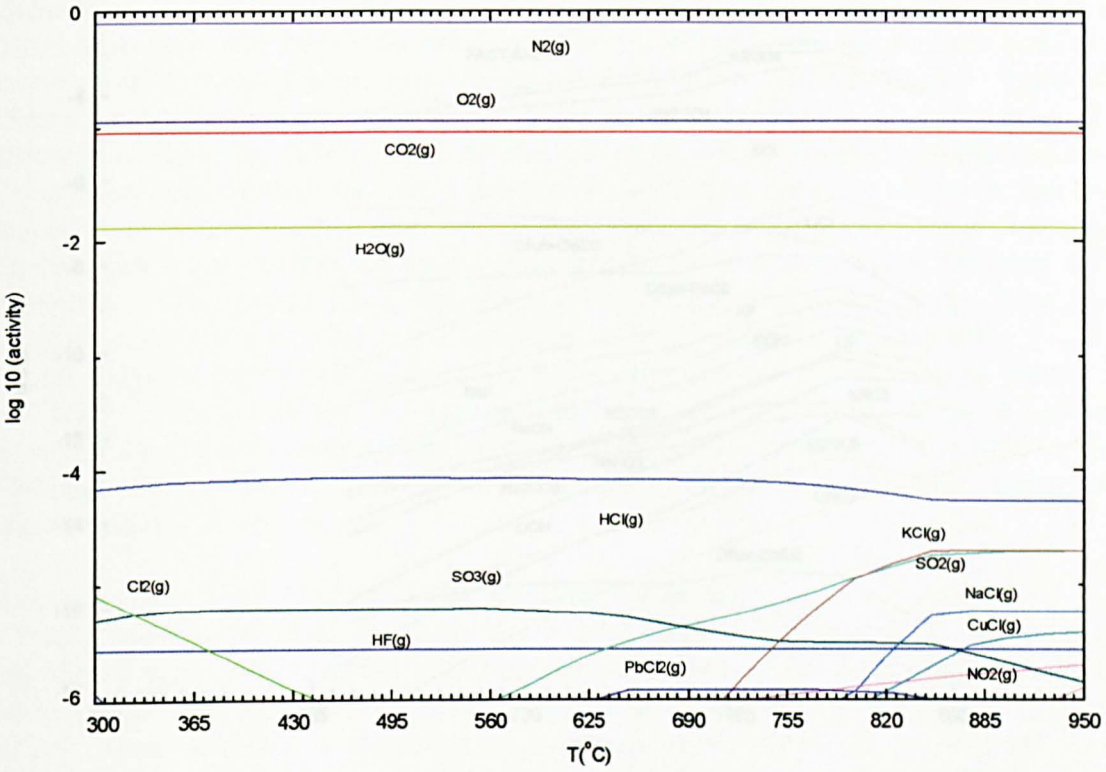


Figure 46: Predicted major gaseous products following scheil cooling of combustion gas from MSW incineration

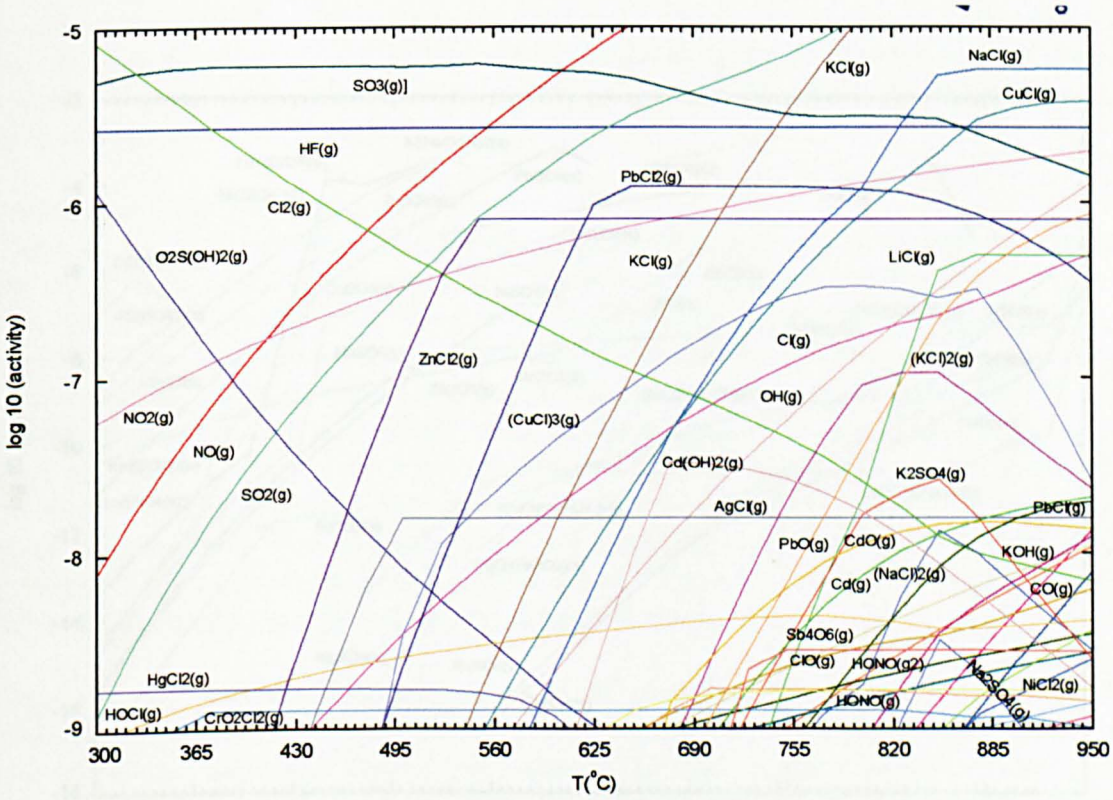


Figure 47: Predicted minor gaseous products following scheil cooling of combustion gas from MSW incineration

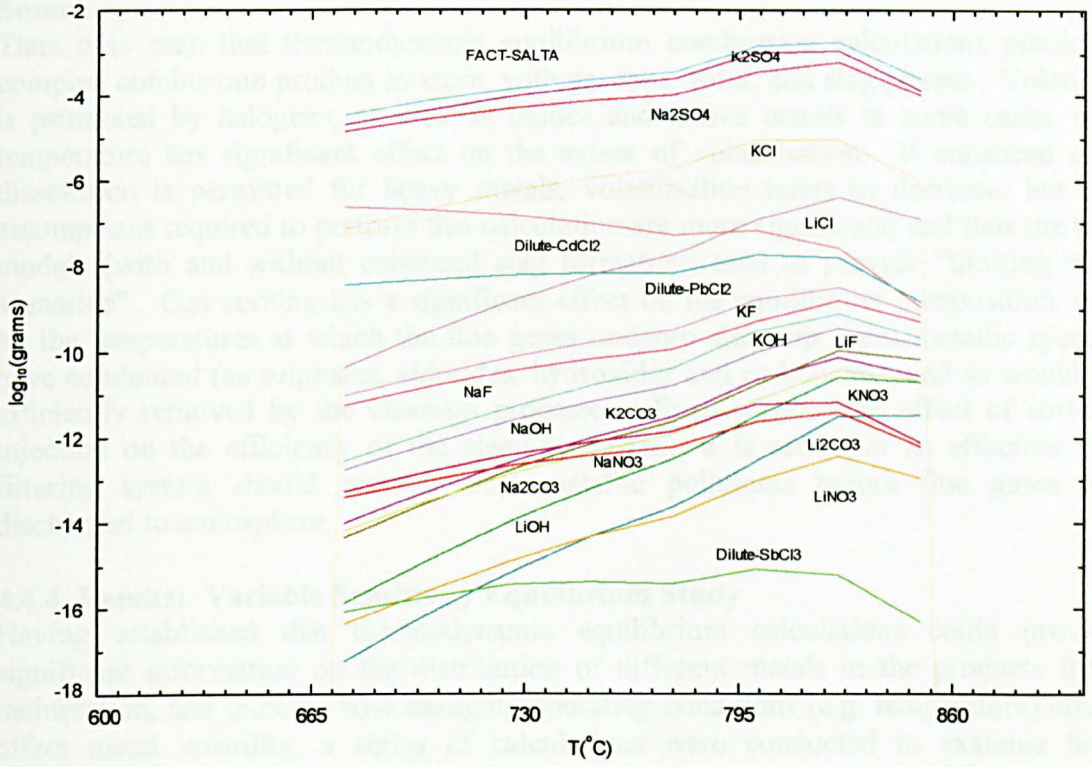


Figure 48: Predicted fused salt products following scheil cooling of combustion gas from MSW incineration

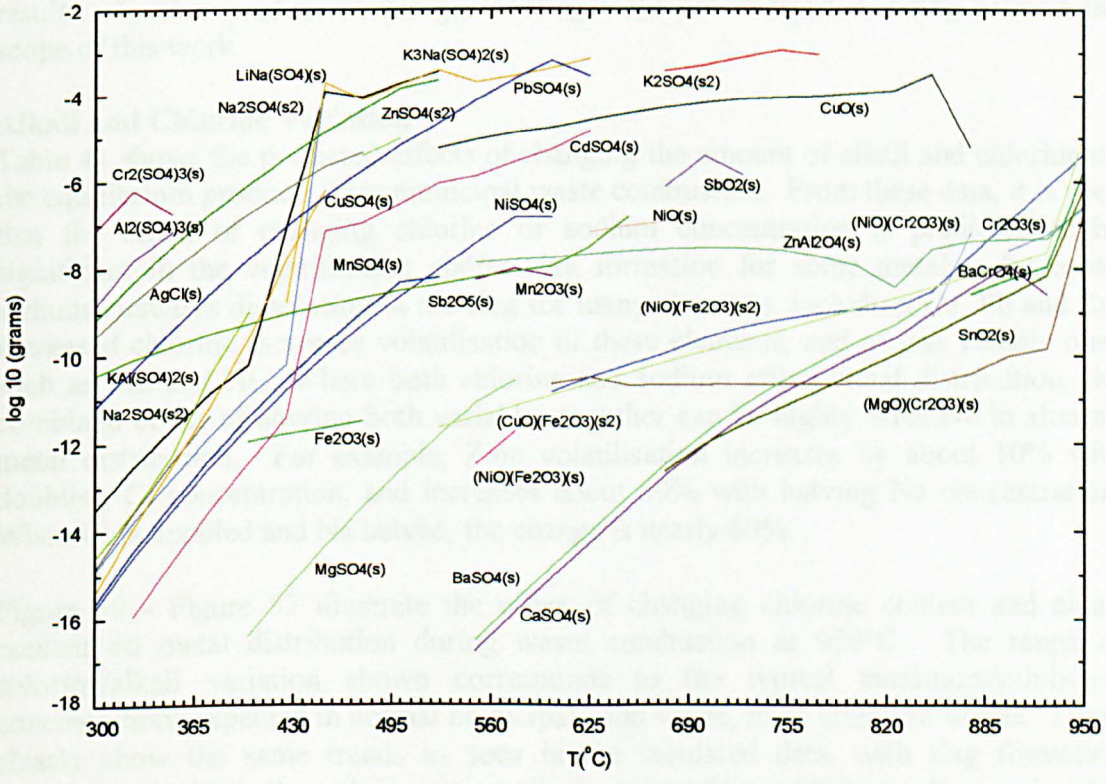


Figure 49: Predicted solid products following scheil cooling of combustion gas from MSW incineration

Summary

Thus it is seen that thermodynamic equilibrium combustion calculations predict a complex combustion product mixture, with gaseous, solid, and slag phases. Volatility is promoted by halogens, as well as oxides and native metals in some cases, and temperature has significant effect on the extent of volatilisation. If enhanced slag dissolution is permitted for heavy metals, volatilisation tends to decrease, but the assumptions required to perform this calculation are more significant, and thus the two models (with and without enhanced slag formation) tend to provide "limiting case scenarios". Gas cooling has a significant effect on the equilibrium composition, and by the temperatures at which the flue gases undergo clean-up, most metallic species have condensed (as sulphates, chlorides, hydroxides and carbonates), and so would be efficiently removed by the clean-up processes. Even without the effect of sorbent injection on the efficiency of the clean-up system, it is seen that an effective bag filtering system should remove most metallic pollutants before flue gases are discharged to atmosphere.

4.4.4 Results: Variable Sensitivity Equilibrium Study

Having established that thermodynamic equilibrium calculations could provide significant information on the distribution of different metals in the products from incineration, and indicate how changing operating conditions (e.g. temperature) could affect metal volatility, a series of calculations were conducted to examine how sensitive the equilibrium product distribution was to variations in different input variables, relating to the furnace operation, and waste input parameters. Calculations were completed at a range of temperatures, but the results presented below are all for predictions at 950°C, as attempts to consider two independent variables simultaneously led to excessive complexity in the results obtained, and the interpretation of those results. Further predictions for gas cooling were not completed, being beyond the scope of this work.

Alkali and Chlorine Variation

Table 41 shows the predicted effects of changing the amount of alkali and chlorine on the equilibrium products from municipal waste combustion. From these data, it is seen that the effect of changing chlorine or sodium concentration is predicted to be significant in the volatilisation and/or slag formation for some metals. Increased sodium increases dissolution in the slag for many elements, including Cu, Pb and Zn. Increased chlorine increases volatilisation of these elements, and of less volatile ones such as Mn and Ni. Where both chlorine and sodium affect metal distribution, the combined effect of altering both variables together can be highly effective in altering metal distribution. For example, Zinc volatilisation increases by about 10% with doubling Cl concentration, and increases about 50% with halving Na concentration. When Cl is doubled and Na halved, the change is nearly 60%.

Figure 50 - Figure 57 illustrate the effect of changing chlorine content and alkali content on metal distribution during waste combustion at 950°C. The range of chlorine/alkali variation shown corresponds to the typical maximum/minimum concentrations expected in normal municipal solid waste, from literature values. These clearly show the same trends as seen in the tabulated data, with slag formation increasing significantly with increasing alkali content (Na and K in the figures, just Na in the table), and with volatile chloride formation tending to increase with increasing chlorine concentration. However, as slag formation affects the composition of solid residues, as well as gaseous products, an increase in slag formation does not always

correspond to a decrease in metal volatilisation, it may just correspond in a reduction in the amount of pure solid compound remaining.

Table 41: Variable sensitivity study: effect of changing chlorine and sodium concentrations in feed waste on equilibrium product distribution at 950°C (wt %)

element	products predicted	typical MSW	twice Cl	half Cl	half Na	twice Na	twice Cl half Na	half Cl twice Na	key species
Ag	gas	100.00	100.00	100.00	100.00	100.00	100.00	100.00	AgCl, Ag
Al	Al in slag	42.90	41.79	43.76	22.22	76.21	21.10	77.74	Al2O3
	pure solid	57.10	58.21	56.23	77.78	23.79	78.90	22.26	CaAl2Si2O8, KAlSi2O6
As	As in slag	100.00	100.00	100.00	100.00	100.00	100.00	100.00	As2O3
Ba	gas	0.01	0.05	0.00	0.01	0.01	0.05	0.00	BaCl2
	pure solid	99.99	99.95	100.00	99.99	99.99	99.95	100.00	BaCrO4(s)
C	gas	100.00	100.00	100.00	100.00	100.00	100.00	100.00	CO2(g), CO (at higher temperatures)
Ca	gas	0.00	0.00	0.00	0.00	0.00	0.00	0.00	CaCl2
	Ca in slag	35.05	32.97	37.15	11.71	70.63	11.17	72.17	CaO
	pure solid	64.95	67.03	62.85	88.29	29.37	88.83	27.83	MgOCaOSi2O4, CaAl2Si2O8, Ca3Fe2Si3O12, CaSiTiO5, (CaO)(MoO3)
Cd	gas	100.00	100.00	100.00	100.00	100.00	100.00	100.00	Cd, CdO, (CdOH)
Cl	gas	100.00	100.00	100.00	100.00	100.00	100.00	100.00	HCl, NaCl, KCl, CuCl, LiCl, ZnCl2, Cl, PbCl2, LiCl, (CuCl)3, Cl2, PbCl, AgCl, ClO
Co	gas	6.52	25.91	1.64	6.23	8.52	25.11	2.08	CoCl2, CoCl3
	pure solid	93.48	74.09	98.36	93.77	91.48	74.89	97.92	(CoO)(Cr2O3), (CoO)(Fe2O3)
Cr	Cr in slag	0.11	0.07	0.16	0.01	0.27	0.00	0.28	Cr2O3, CrO (only at lower temperatures)
	pure solid	99.89	99.93	99.84	99.99	99.73	100.00	99.72	BaCrO4(s), (MgO)(Cr2O3), (CoO)(Cr2O3)
Cu	gas	71.42	85.69	37.67	76.80	56.16	95.33	34.21	CuCl, (CuCl)3, Cu, CuF, CuO
	Cu in slag	28.58	14.31	34.98	8.92	43.84	4.67	56.02	Cu2O
	pure solid	0.00	0.00	27.35	14.29	0.00	0.00	9.77	(CuO)(Fe2O3)
F	gas	100.00	100.00	100.00	100.00	100.00	100.00	100.00	HF, OAlF2, LiF, NaF, KF, CuF
Fe	Fe in slag	0.06	0.05	0.08	0.01	0.19	0.01	0.19	FeO, Fe2O3
	pure solid	99.94	99.95	99.92	99.99	99.81	99.99	99.81	Fe2O3, Ca3Fe2Si3O12, (CuO)(Fe2O3), (NiO)(Fe2O3), (CoO)(Fe2O3)
H	gas	100.00	100.00	100.00	100.00	100.00	100.00	100.00	H2O, HCl, HF, OH
Hg	gas	100.00	100.00	100.00	100.00	100.00	100.00	100.00	Hg, HgCl2
K	gas	8.20	14.92	4.09	5.32	16.65	10.69	8.74	KCl, KOH, (KCl)2, KF
	K in slag	78.19	85.08	64.64	94.68	35.11	89.31	34.21	K2O
	pure solid	13.60	0.00	31.28	0.00	48.24	0.00	57.05	KAlSi2O6
Li	gas	100.00	100.00	100.00	100.00	100.00	100.00	100.00	LiCl, LiOH, LiF, (LiCl)2
Mg	Mg in slag	15.90	14.06	18.15	2.94	49.71	2.82	51.77	MgO
	pure solid	84.10	85.94	81.85	97.06	50.29	97.18	48.23	MgOCaOSi2O4, (MgO)(Cr2O3)
Mn	gas	0.03	0.15	0.01	0.20	0.10	0.84	0.00	MnCl2
	Mn in slag	*99.97*	*99.85*	*99.99*	*99.80*	*99.99*	*99.16*	*100.00*	*MnO*
Mo	pure solid	100.00	100.00	100.00	100.00	100.00	100.00	100.00	(CaO)(MoO3)(s)
N	gas	100.00	100.00	100.00	100.00	100.00	100.00	100.00	N2, NO, N2O
Na	gas	2.71	5.24	1.34	4.69	4.52	9.43	2.40	NaCl, NaOH, (NaCl)2, NaF
	Na in slag	97.29	94.76	98.66	95.32	95.48	90.57	97.60	Na2O
Ni	gas	0.41	4.79	0.14	0.41	0.35	1.52	0.12	NiCl2, Ni(OH)2, NiCl
	Ni in slag	6.16	4.79	8.15	0.58	19.53	0.51	20.29	NiO
	pure solid	93.44	93.71	91.71	99.01	80.11	97.98	79.59	(NiO)(Fe2O3)(s
O	gas	99.51	99.51	99.51	99.51	99.50	99.51	99.50	O2, CO2, H2O, NO, SO2, SO3
	O in slag	0.25	0.25	0.25	0.15	0.35	0.14	0.36	SiO2, Al2O3, CaO, Na2O, K2O, Ti2O, N2O
	pure solid	0.24	0.25	0.24	0.34	0.15	0.34	0.15	Fe2O3, MgOCaOSi2O4, CaAl2Si2O8, KAlSi2O6, Sio2, Ca3Fe2Si3O12, CaSiTiO5, BaCrO4, (NiO)(Fe2O3), SnO2, (MgO)(Cr2O3)
Pb	gas	84.83	93.36	76.64	95.43	83.22	98.09	77.78	PbO, PbCl2, PbCl, Pb
	Pb in slag	15.17	6.64	23.36	4.57	16.78	1.91	22.22	PbO
S	gas	100.00	100.00	100.00	100.00	100.00	100.00	100.00	SO2, SO3, SO
Sb	gas	8.50	10.08	8.32	8.51	8.46	10.11	8.31	(SbO2H2), SbCl3, SbOH
	pure solid	91.50	89.92	91.68	91.49	91.54	89.89	91.69	SbO2
Si	gas	0.00	0.00	0.00	0.00	0.00	0.00	0.00	OSiF2
	Si in slag	64.15	64.28	63.93	41.81	80.55	39.55	80.84	SiO2
	pure solid	35.85	35.72	36.07	58.19	19.45	60.45	19.16	MgOCaOSi2O4, CaAl2Si2O8, KAlSi2O6, Ca3Fe2Si3O12, CaSiTiO5, Zn2SiO4
Sn	pure solid	100.00	100.00	100.00	100.00	100.00	100.00	100.00	SnO2
Ti	gas	0.00	0.00	0.00	0.00	0.00	0.00	0.00	TiOCl2(g)
	Ti in slag	*37.36*	*32.91*	*41.15*	*11.24*	*100.00*	*10.35*	*100.00*	*TiO2, Ti2O3*
	pure solid	62.64	67.09	58.85	88.76	0.00	89.65	0.00	CaSiTiO5
Zn	gas	10.82	43.39	2.73	10.67	8.46	42.98	2.16	ZnCl2, Zn
	Zn in slag	41.30	34.87	50.39	5.51	91.54	5.25	97.84	ZnO
	pure solid	47.88	21.74	46.88	83.83	0.00	51.77	0.00	Zn2SiO4

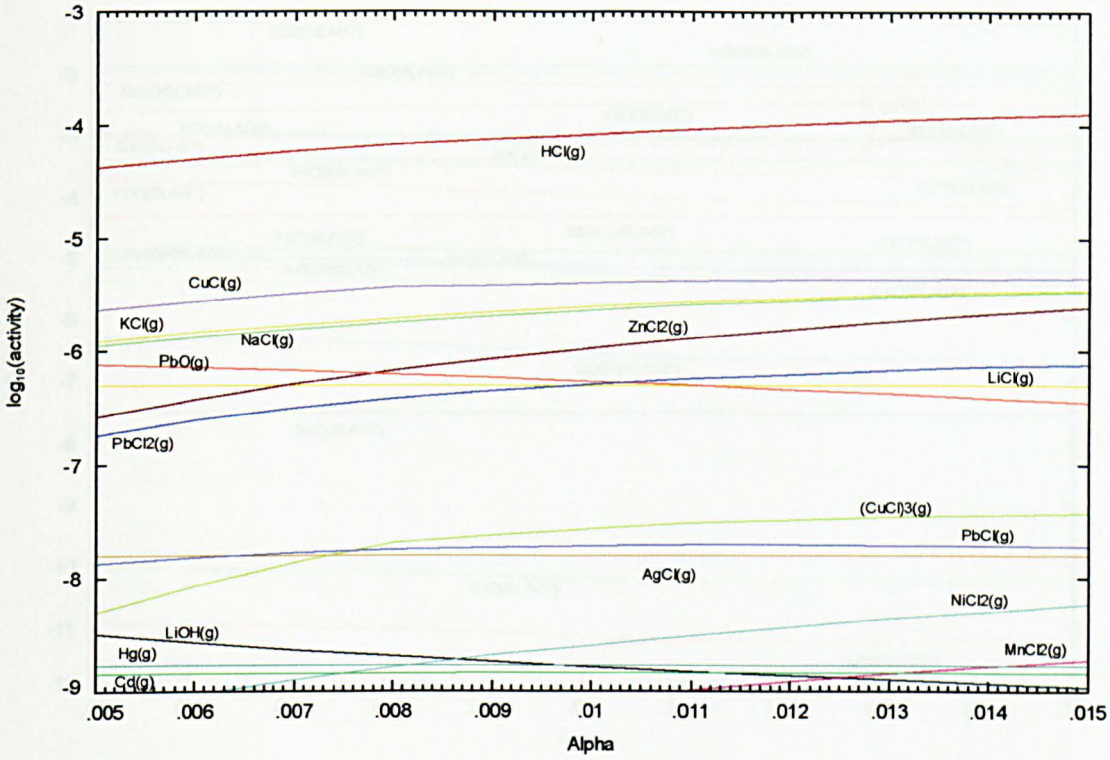


Figure 50: Major gaseous species from MSW combustion with a range of chlorine content (Alpha indicates total chlorine)

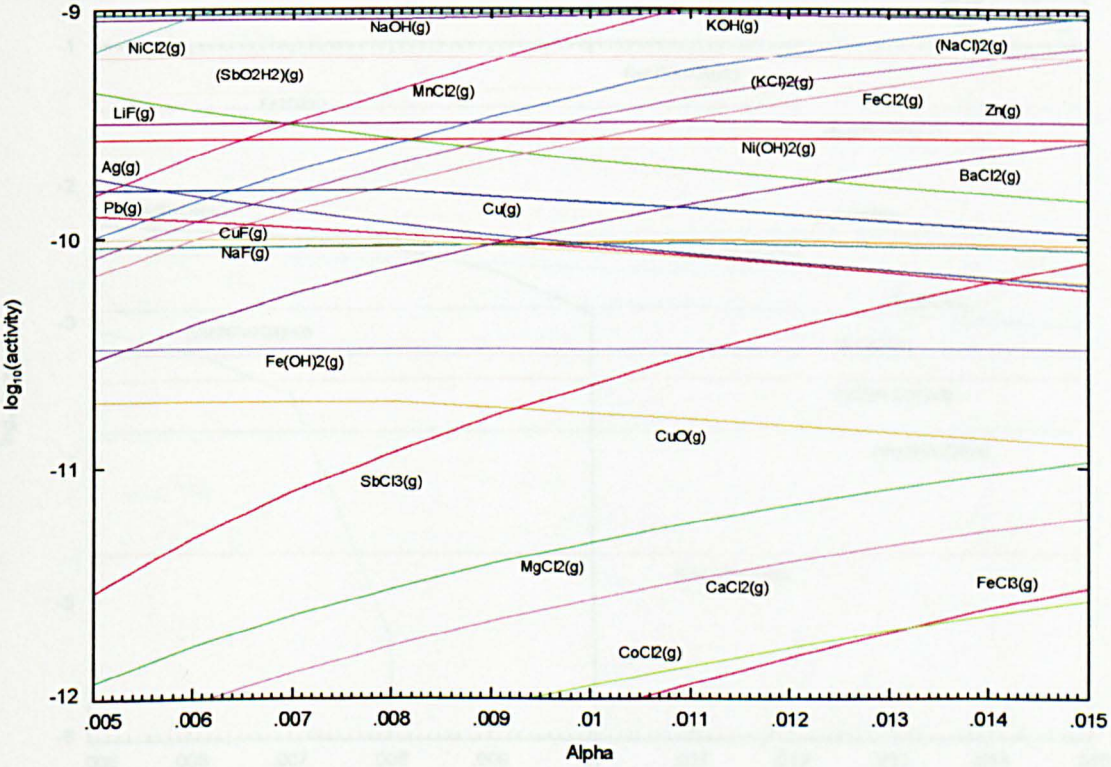


Figure 51: Minor gaseous species from MSW combustion with a range of total chlorine content (Alpha indicates total chlorine)

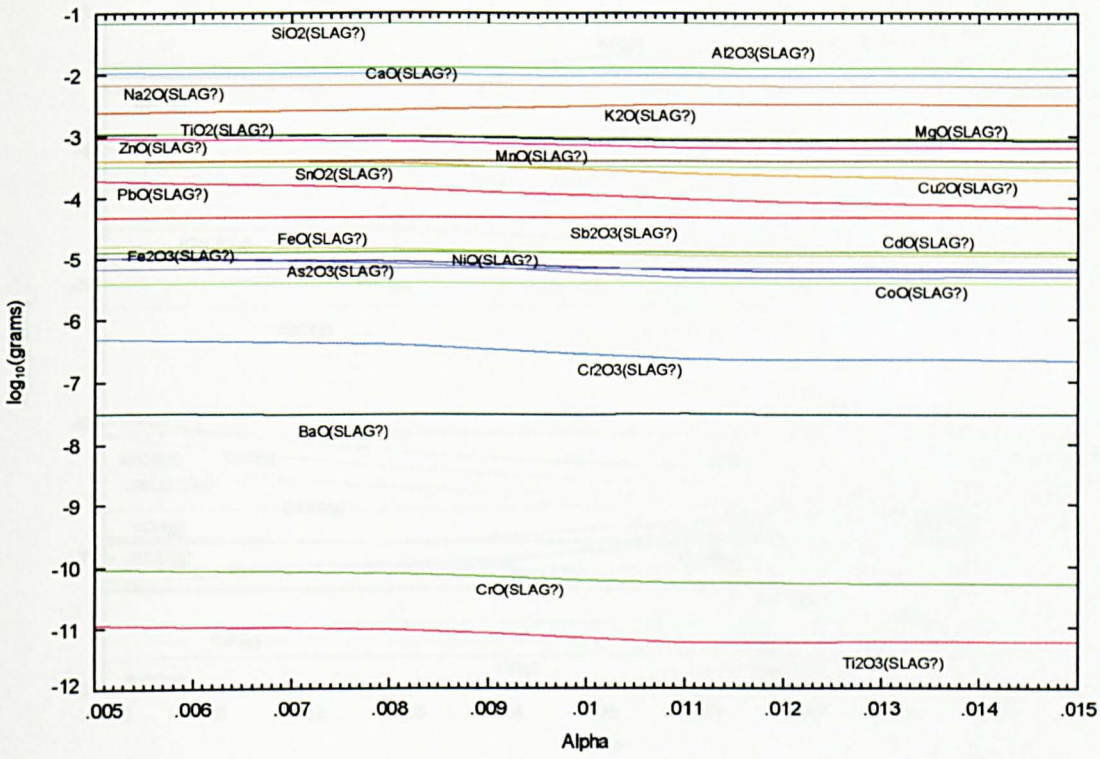


Figure 52: Slag components from MSW combustion with a range of total chlorine content (Alpha indicates total chlorine)

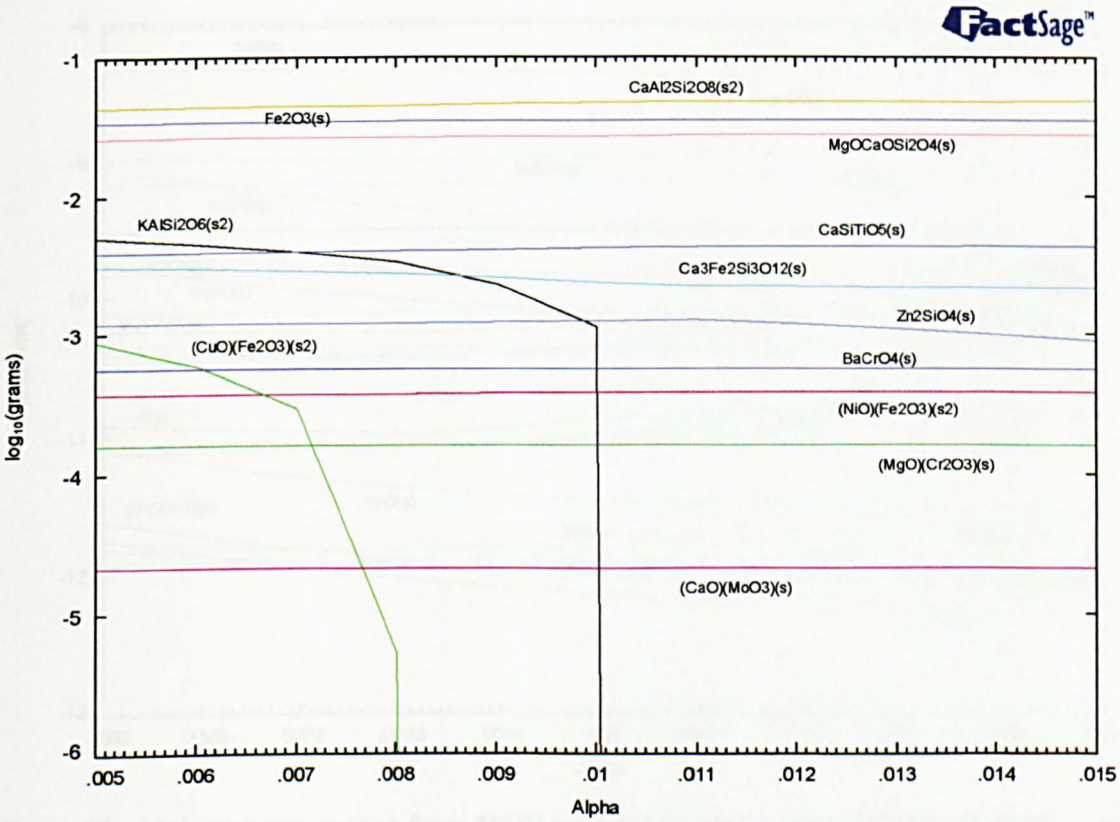


Figure 53: Solid compounds from MSW combustion with a range of chlorine content (Alpha indicates total chlorine)

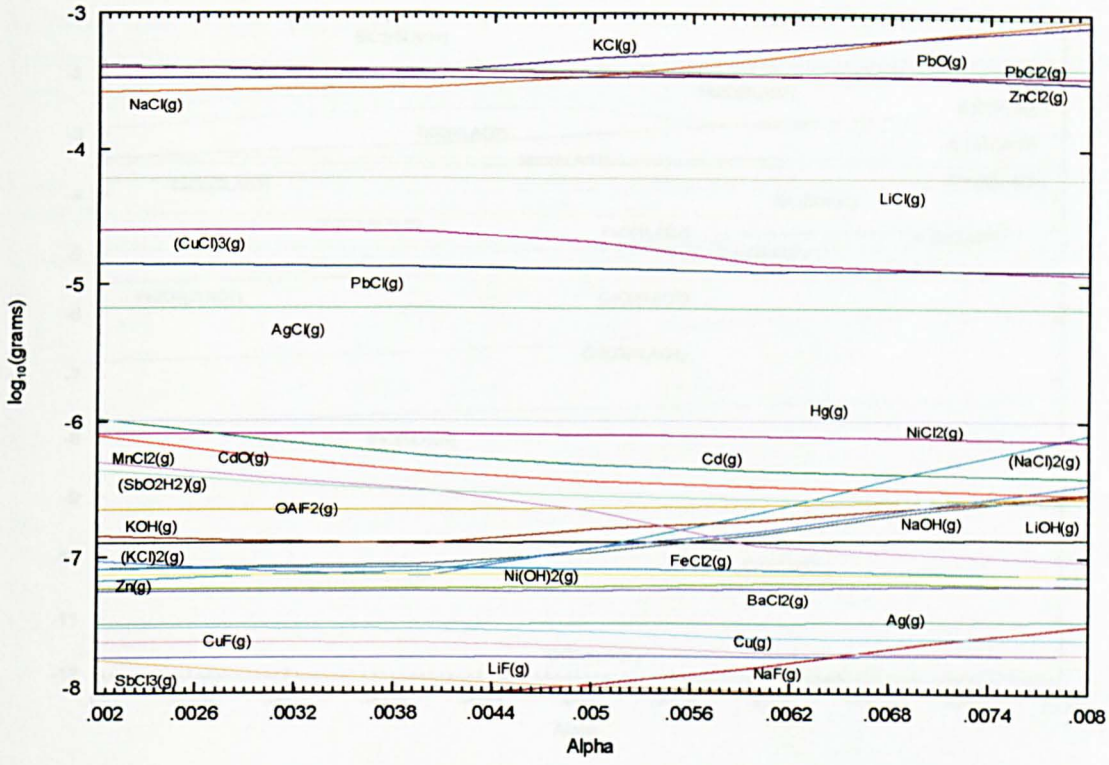


Figure 54: Major gaseous species from MSW combustion with a range of total alkali (Na + K) content (Alpha indicates the sodium and 0.6 Alpha the potassium content)

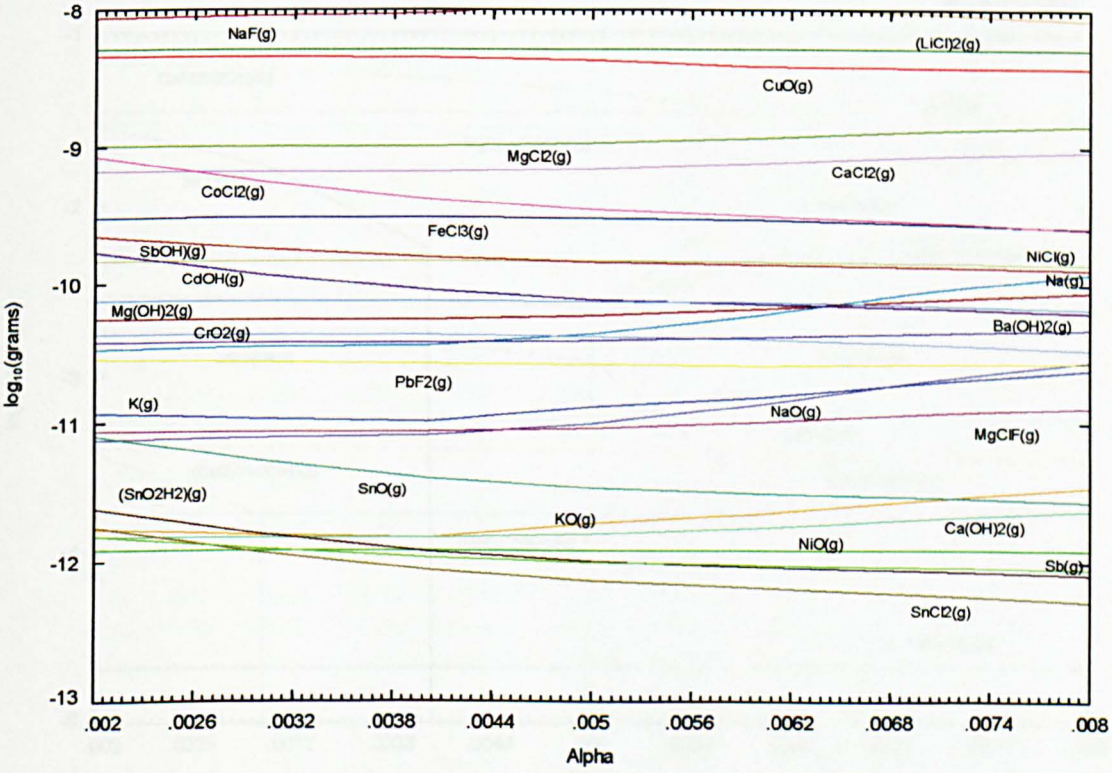


Figure 55: Major gaseous species from MSW combustion with a range of total alkali (Na + K) content (Alpha indicates the sodium and 0.6 Alpha the potassium content)

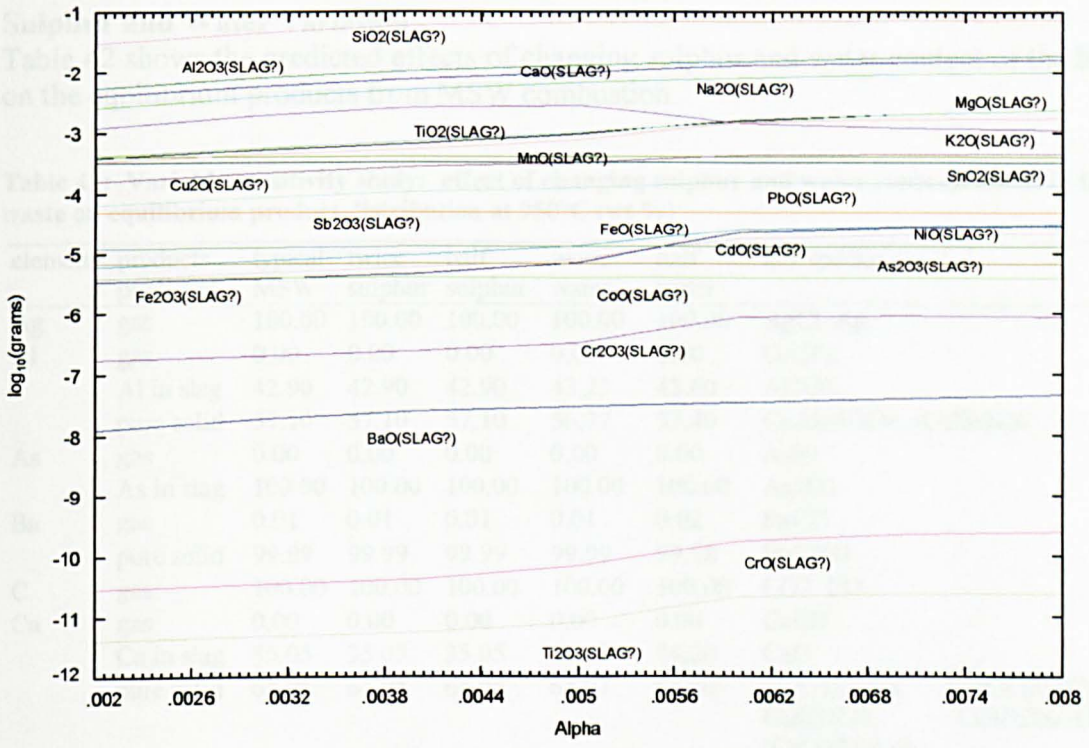


Figure 56: Major oxide slag components from MSW combustion with a range of total alkali (Na + K) content (Alpha indicates the sodium and 0.6 Alpha the potassium content)

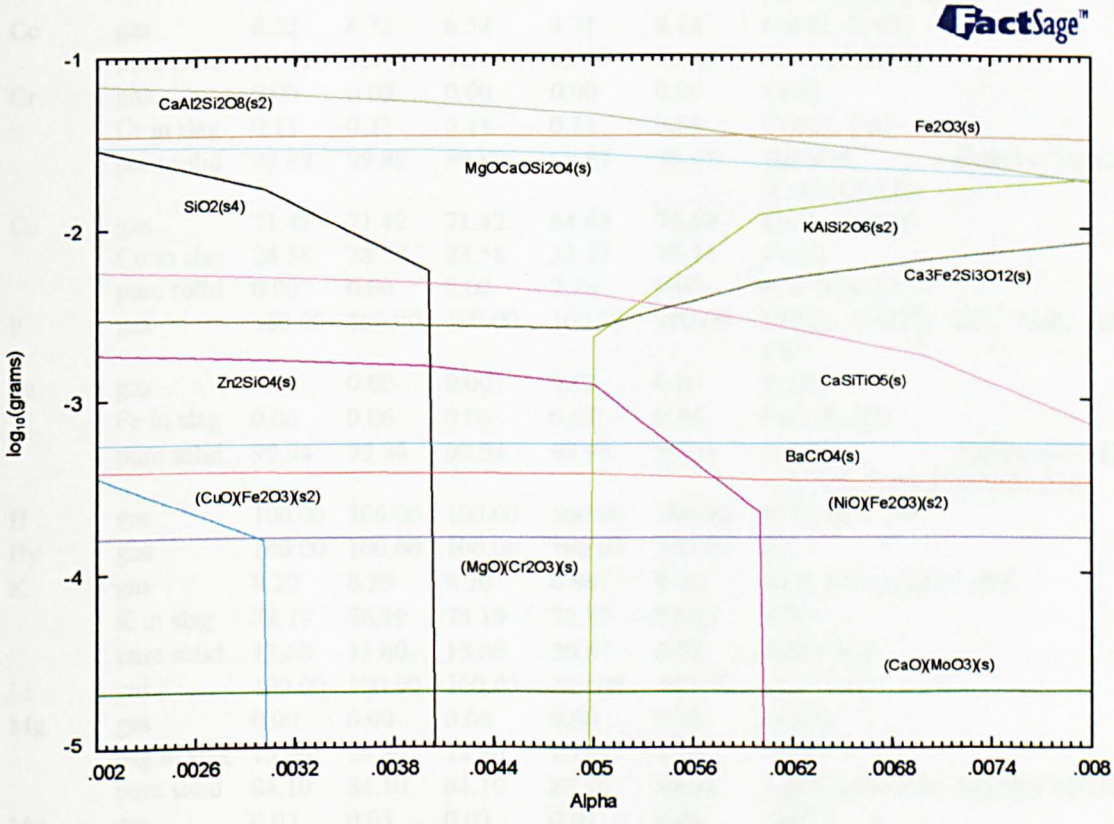


Figure 57: Major solid species from MSW combustion with a range of total alkali (Na + K) content (Alpha indicates the sodium and 0.6 Alpha the potassium content)

Sulphur and Water Variation

Table 42 shows the predicted effects of changing sulphur and water content of the fuel on the equilibrium products from MSW combustion.

Table 42: Variable sensitivity study: effect of changing sulphur and water concentrations in feed waste on equilibrium product distribution at 950°C (wt %)

element	products predicted	typical MSW	twice sulphur	half sulphur	twice water	half water	key species
Ag	gas	100.00	100.00	100.00	100.00	100.00	AgCl, Ag
Al	gas	0.00	0.00	0.00	0.00	0.00	OAlF2
	Al in slag	42.90	42.90	42.90	43.23	42.60	Al2O3
	pure solid	57.10	57.10	57.10	56.77	57.40	CaAl2Si2O8, KAlSi2O6
As	gas	0.00	0.00	0.00	0.00	0.00	AsF3
	As in slag	100.00	100.00	100.00	100.00	100.00	As2O3
Ba	gas	0.01	0.01	0.01	0.01	0.02	BaCl2
	pure solid	99.99	99.99	99.99	99.99	99.98	BaCrO4
C	gas	100.00	100.00	100.00	100.00	100.00	CO2, CO
Ca	gas	0.00	0.00	0.00	0.00	0.00	CaCl2
	Ca in slag	35.05	35.05	35.05	35.93	34.20	CaO
	pure solid	64.95	64.95	64.95	64.07	65.80	CaAl2Si2O8, MgOCaOSi2O4, CaSiTiO5, Ca3Fe2Si3O12, (CaO)(MoO3)
Cd	gas	100.00	100.00	100.00	100.00	100.00	Cd, CdO, (CdOH)
Cl	gas	100.00	100.00	100.00	100.00	100.00	HCl, CuCl, KCl, NaCl, ZnCl2, PbCl2, Cl, LiCl, (CuCl)3, Cl2, PbCl, AgCl, ClO
Co	gas	6.52	6.52	6.52	4.71	8.14	CoCl2, CoCl3
	pure solid	93.48	93.48	93.48	95.29	91.86	(CoO)(Cr2O3)
Cr	gas	0.00	0.00	0.00	0.00	0.00	CrO2
	Cr in slag	0.11	0.11	0.11	0.13	0.09	Cr2O3, CrO
	pure solid	99.89	99.89	99.89	99.87	99.91	BaCrO4, (MgO)(Cr2O3), (CoO)(Cr2O3)
Cu	gas	71.42	71.42	71.42	64.65	74.89	CuCl, (CuCl)3
	Cu in slag	28.58	28.58	28.58	32.57	25.11	Cu2O
	pure solid	0.00	0.00	0.00	2.78	0.00	(CuO)(Fe2O3)
F	gas	100.00	100.00	100.00	100.00	100.00	HF(g), OAlF2, LiF, NaF, KF, CuF
Fe	gas	0.00	0.00	0.00	0.00	0.00	FeCl2
	Fe in slag	0.06	0.06	0.06	0.07	0.05	FeO, Fe2O3
	pure solid	99.94	99.94	99.94	99.93	99.95	Fe2O3, Ca3Fe2Si3O12, (NiO)(Fe2O3), (CuO)(Fe2O3)
H	gas	100.00	100.00	100.00	100.00	100.00	H2O, HCl, HF
Hg	gas	100.00	100.00	100.00	100.00	100.00	Hg
K	gas	8.20	8.20	8.20	6.96	9.20	KCl, KOH, (KCl)2, KF
	K in slag	78.19	78.19	78.19	72.17	84.25	K2O
	pure solid	13.60	13.60	13.60	20.87	6.55	KAlSi2O6
Li	gas	100.00	100.00	100.00	100.00	100.00	LiCl, LiOH, LiF
Mg	gas	0.00	0.00	0.00	0.00	0.00	MgCl2
	Mg in slag	15.90	15.90	15.90	16.84	15.02	MgO
	pure solid	84.10	84.10	84.10	83.16	84.98	MgOCaOSi2O4, (MgO)(Cr2O3)
Mn	gas	0.03	0.03	0.03	0.02	0.04	MnCl2
	Mn in slag	99.97	99.97	99.97	99.98	99.96	MnO
Mo	gas	0.00	0.00	0.00	0.00	0.00	MoO
	pure solid	100.00	100.00	100.00	100.00	100.00	(CaO)(MoO3)
N	gas	100.00	100.00	100.00	100.00	100.00	N2, NO
Na	gas	2.71	2.71	2.71	2.28	3.07	NaCl, NaOH
	Na in slag	97.29	97.29	97.29	97.72	96.93	Na2O

element	products predicted	typical MSW	twice sulphur	half sulphur	twice water	half water	key species
Ni	gas	0.41	0.41	0.41	0.33	0.48	NiCl2, Ni(OH)2, NiCl
	Ni in slag	6.16	6.16	6.16	7.02	5.40	NiO
	pure solid	93.44	93.44	93.44	92.66	94.12	(NiO)(Fe2O3)
O	gas	99.51	99.51	99.51	99.51	99.50	O2, CO2, H2O, NO, SO2
	O in slag	0.25	0.25	0.25	0.25	0.25	SiO2, Al2O3, CaO, Na2O, K2O, Ti2O
	pure solid	0.24	0.24	0.24	0.24	0.25	CaAl2Si2O8(s2), MgOCaOSi2O4, Fe2O3
Pb	gas	84.83	84.83	84.83	82.25	86.83	PbO, PbCl2, PbCl
	Pb in slag	15.17	15.17	15.17	17.75	13.17	PbO
S	gas	100.00	100.00	100.00	100.00	100.00	SO2, SO3
Sb	gas	8.50	8.50	8.50	12.10	6.74	(SbO2H2), SbCl3, SbOH
	pure solid	91.50	91.50	91.50	87.90	93.26	SbO2
Si	gas	0.00	0.00	0.00	0.00	0.00	OSiF2
	Si in slag	64.15	64.15	64.15	64.06	64.24	SiO2
	pure solid	35.85	35.85	35.85	35.94	35.76	CaAl2Si2O8, MgOCaOSi2O4, CaSiTiO5, Ca3Fe2Si3O12, KAlSi2O6, Zn2SiO4
Sn	gas	0.00	0.00	0.00	0.00	0.00	SnO, (SnO2H2), SnCl2
	pure solid	100.00	100.00	100.00	100.00	100.00	SnO2
Ti	gas	0.00	0.00	0.00	0.00	0.00	TiOCl2
	Ti in slag	37.36	37.36	37.36	39.01	35.84	TiO2
	pure solid	62.64	62.64	62.64	60.99	64.16	CaSiTiO5
Zn	gas	10.82	10.82	10.82	7.83	13.46	ZnCl2, Zn
	Zn in slag	41.30	41.30	41.30	45.11	37.84	ZnO
	pure solid	47.88	47.88	47.88	47.06	48.70	Zn2SiO4

Compared with the effect of changing chlorine or alkali content of the waste input, the effect of changing the sulphur or water content of the waste has only a small effect on product composition. In contrast to previous predictions (Linak and Wendt, 1993), these more complex thermodynamic equilibrium calculations estimate the effect of a doubling or halving of sulphur content to be minimal on the distribution of any of the metals (previous calculations predicted the effects on equilibrium to be small for most metals, but significant for some, such as lead, as it was thought that lead sulphate would be favoured over lead chloride). All of the sulphur is found as non-metallic gases (mainly SO_2, with a trace of SO_3). However, it is important to remember that the slag model did not include sulphate or sulphite components, and the ability to include these could alter the equilibrium products significantly. The water content of the fuel has a discernible, but small effect on metal distribution, with higher water content tending to increase slag formation, and decrease volatilisation, with the exception of Sb, where the reverse is true (presumably due to the volatilisation of Sb via the compound (SbO_2H_2).. Figure 58 - Figure 60 illustrate the predicted effects on the equilibrium products of changing the water concentration over the range typically expected in MSW.

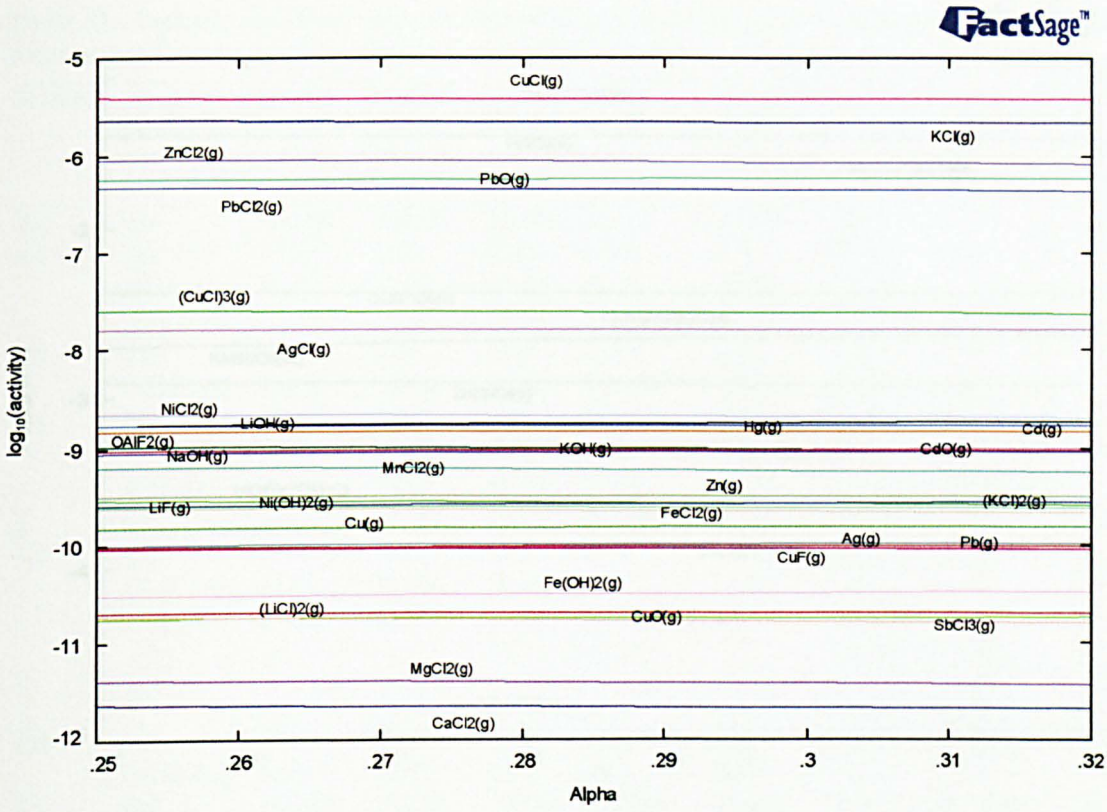


Figure 58: Gaseous compounds from MSW combustion with a range of water concentrations (alpha indicates water concentration, in the range 25-32%)

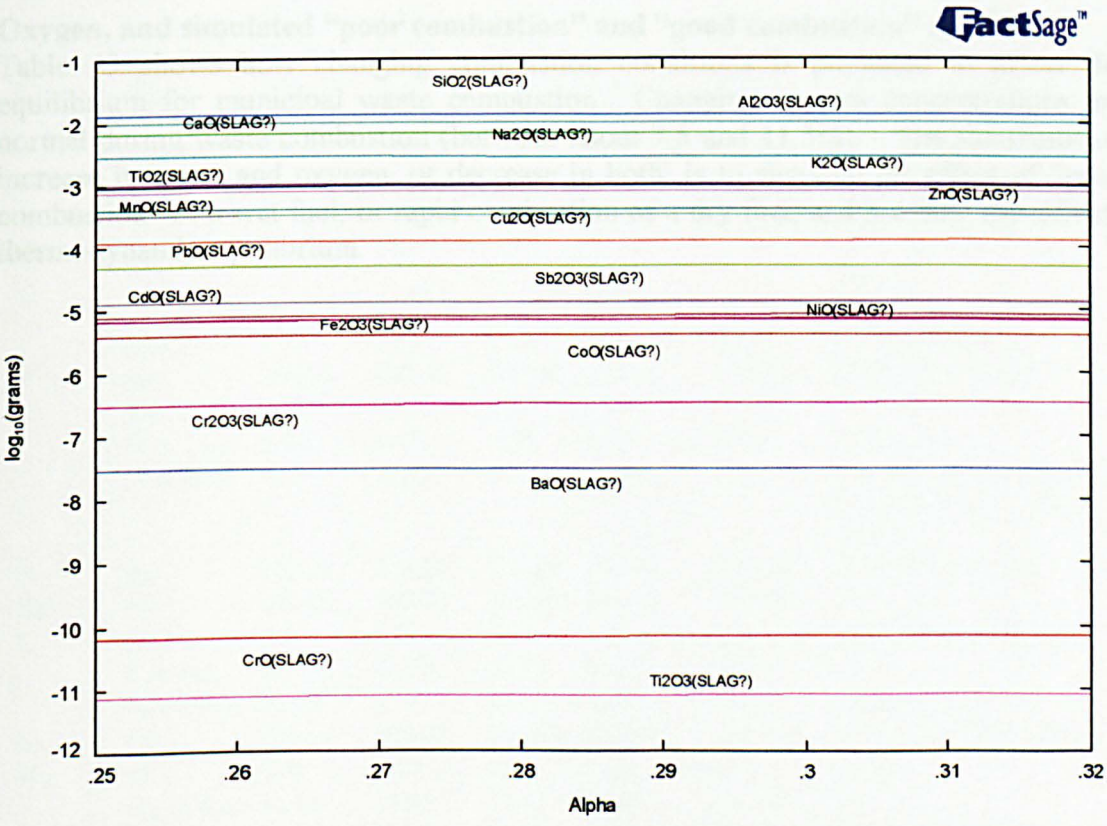


Figure 59: Oxide slag components from MSW combustion with a range of water concentrations (alpha indicates water concentration, in the range 25-32%)

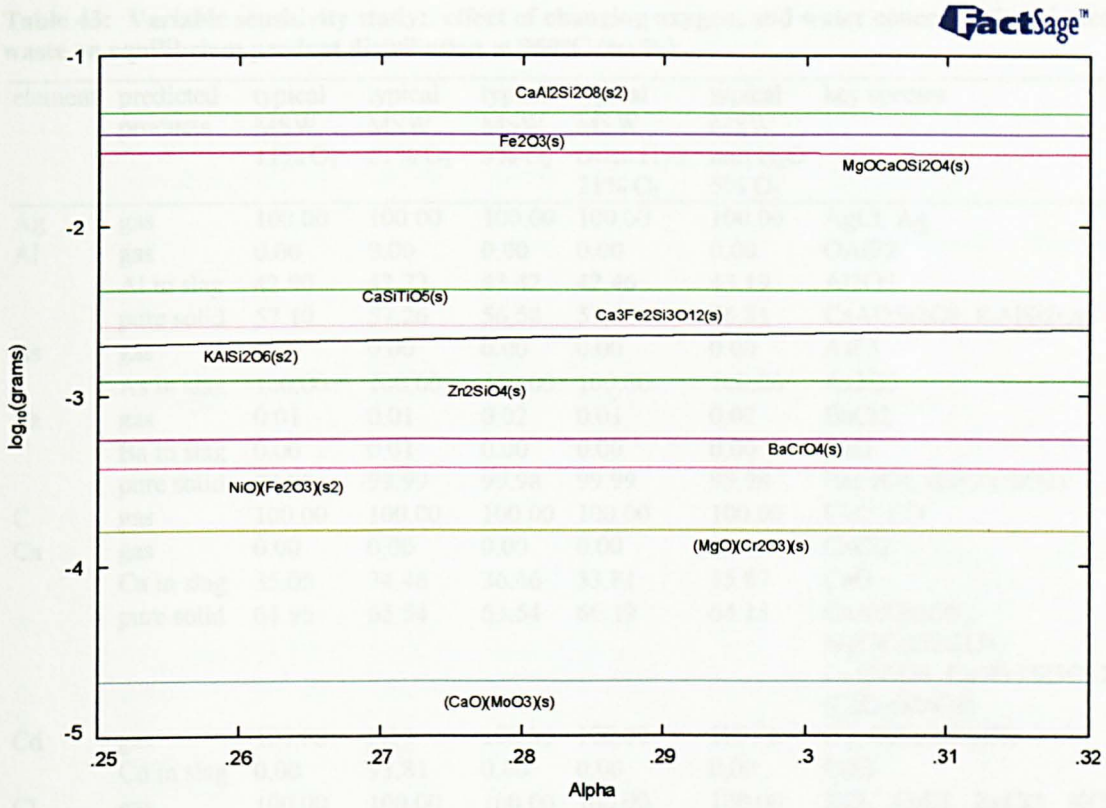


Figure 60: Pure solid components from MSW combustion with a range of water concentrations (alpha indicates water concentration, in the range 25-32%)

Oxygen, and simulated "poor combustion" and "good combustion" regions

Table 43 shows how changing combustion conditions is predicted to affect the equilibrium for municipal waste combustion. Changing oxygen concentrations are normal during waste combustion (between about 7.5 and 11.5%). The simultaneous increase in water and oxygen, or decrease in both, is to simulate the effect of "poor combustion" of a wet fuel, or rapid combustion of a dry fuel, and see how this affects thermodynamic equilibrium.

Table 43: Variable sensitivity study: effect of changing oxygen, and water concentrations in feed waste on equilibrium product distribution at 950°C (wt %)

element	predicted products	typical MSW 11% O_2	typical MSW 21% O_2	typical MSW 5% O_2	typical MSW twice H_2O 21% O_2	typical MSW half H_2O 5% O_2	key species
Ag	gas	100.00	100.00	100.00	100.00	100.00	AgCl, Ag
Al	gas	0.00	0.00	0.00	0.00	0.00	OAlF2
	Al in slag	42.90	42.73	43.42	42.46	43.19	Al2O3
	pure solid	57.10	57.26	56.58	57.54	56.81	CaAl2Si2O8, KAlSi2O6
As	gas	0.00	0.00	0.00	0.00	0.00	AsF3
	As in slag	100.00	100.00	100.00	100.00	100.00	As2O3
Ba	gas	0.01	0.01	0.02	0.01	0.02	BaCl2
	Ba in slag	0.00	0.01	0.00	0.00	0.00	BaO
	pure solid	99.99	99.99	99.98	99.99	99.98	BaCrO4, (BaO)(SiO2)
C	gas	100.00	100.00	100.00	100.00	100.00	CO2, CO
Ca	gas	0.00	0.00	0.00	0.00	0.00	CaCl2
	Ca in slag	35.05	34.46	36.46	33.81	35.87	CaO
	pure solid	64.95	65.54	63.54	66.19	64.13	CaAl2Si2O8, MgOCaOSi2O4, CaSiTiO5, Ca3Fe2Si3O12, (CaO)(MoO3)
Cd	gas	100.00	6.19	100.00	100.00	100.00	Cd, CdO, (CdOH)
	Cd in slag	0.00	93.81	0.00	0.00	0.00	CdO
Cl	gas	100.00	100.00	100.00	100.00	100.00	HCl, CuCl, ZnCl2, KCl, NaCl, PbCl2, Cl, LiCl, (CuCl)3, Cl2, PbCl, AgCl, ClO
Co	gas	6.52	0.01	6.70	4.54	8.37	CoCl2, CoCl3
	Co in slag	0.00	0.00	0.00	0.00	0.00	CoO
	pure solid	93.48	99.99	93.30	95.46	91.63	(CoO)(Cr2O3)
Cr	gas	0.00	0.00	0.00	0.00	0.00	CrO2
	Cr in slag	0.11	0.09	0.15	0.08	0.13	Cr2O3
	pure solid	99.89	99.91	99.85	99.92	99.87	(MgO)(Cr2O3), (CoO)(Cr2O3), BaCrO4, (CoO)(Cr2O3)
Cu	gas	71.42	68.00	64.36	73.19	67.96	CuCl, (CuCl)3, Cu, CuF, CuO
	Cu in slag	28.58	24.31	35.64	23.32	32.04	Cu2O
	pure solid	0.00	7.69	0.00	3.49	0.00	(CuO)(Fe2O3)
F	gas	100.00	100.00	100.00	100.00	100.00	HF(g), OAlF2, LiF
Fe	gas	0.00	0.00	0.00	0.00	0.00	FeCl2
	Fe in slag	0.06	0.05	0.08	0.04	0.08	FeO, Fe2O3
	pure solid	99.94	99.95	99.92	99.96	99.92	Fe2O3(s), Ca3Fe2Si3O12, (NiO)(Fe2O3), (CuO)(Fe2O3)
H	gas	100.00	100.00	100.00	100.00	100.00	H2O, HCl, HF, OH
Hg	gas	100.00	100.00	100.00	100.00	100.00	Hg
K	gas	8.20	8.77	6.43	9.55	7.19	KCl, KOH, (KCl)2, KF
	K in slag	78.19	83.20	68.59	86.87	72.48	K2O
	pure solid	13.60	8.03	24.99	3.58	20.33	KAlSi2O6(s2)
Li	gas	100.00	100.00	100.00	100.00	100.00	LiCl, LiOH, LiF, (LiCl)2
Mg	gas	0.00	0.00	0.00	0.00	0.00	MgCl2
	Mg in slag	15.90	15.25	17.41	14.64	16.77	MgO
	pure solid	84.10	84.75	82.59	85.36	83.23	MgOCaOSi2O4(s), (MgO)(Cr2O3)
Mn	gas	0.03	0.03	0.03	0.02	0.04	MnCl2(g)
	Mn in slag	99.97	99.97	99.97	99.98	99.96	MnO
Mo	gas	0.00	0.00	0.00	0.00	0.00	MoO

element	predicted products	typical MSW 11% O_2	typical MSW 21% O_2	typical MSW 5% O_2	typical MSW twice H_2O 21% O_2	typical MSW half H_2O 5% O_2	key species
	Mo in slag	0.00	0.00	0.00	0.00	0.00	
	pure solid	100.00	100.00	100.00	100.00	100.00	(CaO)(MoO3)
N	gas	100.00	100.00	100.00	100.00	100.00	N2
Na	gas	2.71	2.91	2.09	3.21	2.35	NaCl, NaOH, (NaCl)2, NaF
	Na in slag	97.29	97.09	97.91	96.79	97.65	Na2O
Ni	gas	0.41	0.40	0.42	0.31	0.50	NiCl2, Ni(OH)2, NiCl
	Ni in slag	6.16	5.53	7.60	5.08	6.96	NiO
	pure solid	93.44	94.07	91.99	94.61	92.54	(NiO)(Fe2O3)
O	gas	99.51	99.69	99.20	99.80	99.19	CO2, O2, H2O, NO, SO2
	O in slag	0.25	0.16	0.41	0.10	0.41	SiO2, Al2O3, CaO, Na2O, K2O, Ti2O
	pure solid	0.24	0.15	0.40	0.10	0.40	CaAl2Si2O8, MgOCaOSi2O4, Fe2O3, KAlSi2O6, CaSiTiO5
Pb	gas	84.83	86.28	80.06	89.44	82.65	PbCl2, PbO, PbCl
	Pb in slag	15.17	13.72	19.94	10.56	17.35	PbO
S	gas	100.00	100.00	100.00	100.00	100.00	SO2, SO3
Sb	gas	8.50	0.48	12.64	8.74	10.06	(SbO2H2), SbCl3, SbOH
	Sb in slag	0.00	0.00	0.00	0.00	0.00	
	pure solid	91.50	99.52	87.36	91.26	89.94	SbO2
Si	gas	0.00	0.00	0.00	0.00	0.00	OSiF2
	Si in slag	64.15	64.25	64.00	64.22	64.05	SiO2
	pure solid	35.85	35.75	36.00	35.78	35.95	CaAl2Si2O8, MgOCaOSi2O4, KAlSi2O6, CaSiTiO5, Ca3Fe2Si3O12, Zn2SiO4, (BaO)(SiO2)
Sn	gas	0.00	0.00	0.00	0.00	0.00	SnO, (SnO2H2), SnCl2
	Sn in slag	0.00	0.00	0.00	0.00	0.00	SnO2
	pure solid	100.00	100.00	100.00	100.00	100.00	SnO2
Ti	gas	0.00	0.00	0.00	0.00	0.00	TiOCl2
	Ti in slag	37.36	36.16	40.08	35.17	38.88	TiO2
	pure solid	62.64	63.84	59.92	64.83	61.12	CaSiTiO5
Zn	gas	10.82	10.79	11.16	7.50	13.92	ZnCl2
	Zn in slag	41.30	38.67	47.57	36.35	44.87	ZnO
	pure solid	47.88	50.54	41.27	56.15	41.21	Zn2SiO4

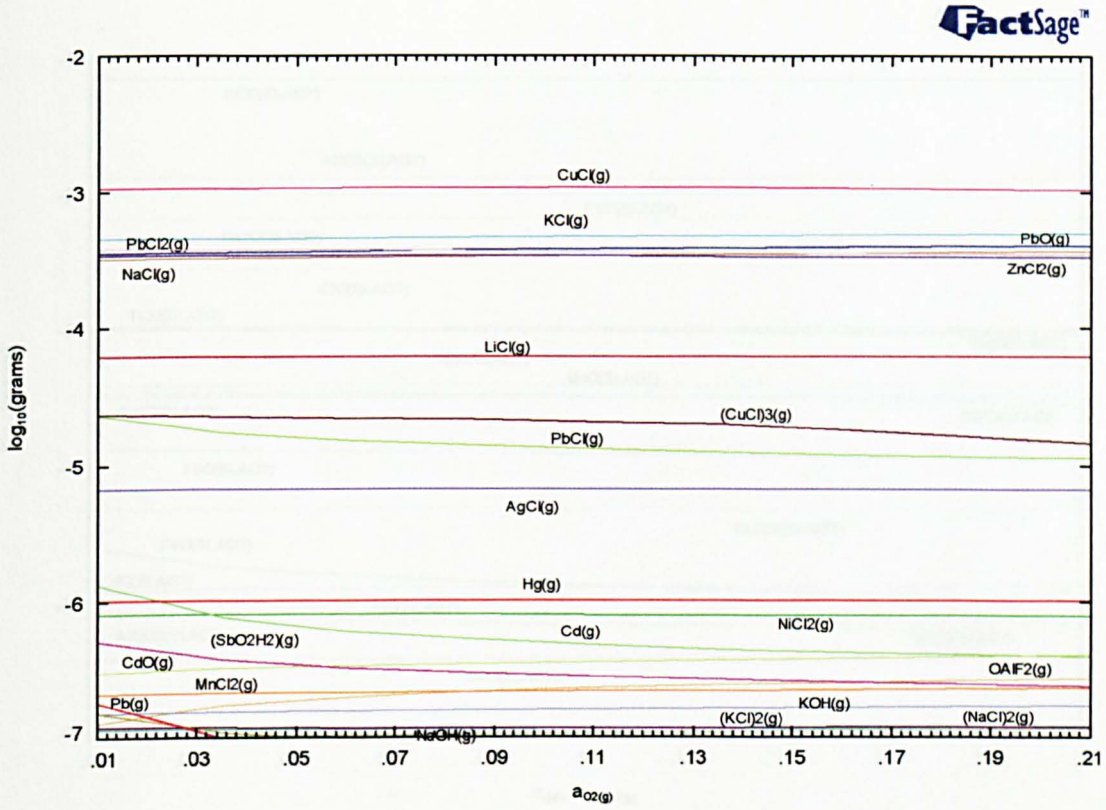


Figure 61: Major gaseous compounds from MSW combustion with a range of oxygen concentrations (shown for oxygen activities between 0.01 and 0.21, i.e. 1-21%)

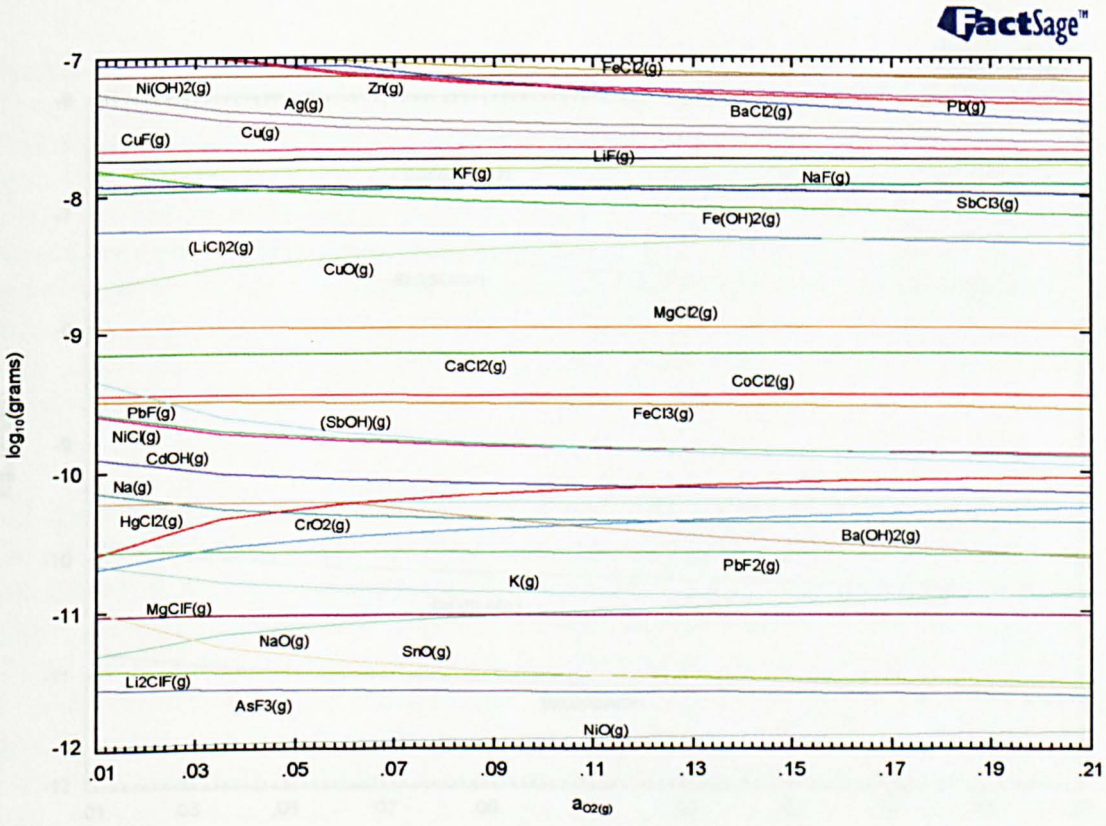


Figure 62: Minor gaseous compounds from MSW combustion with a range of oxygen concentrations (shown for oxygen activities between 0.01 and 0.21, i.e. 1-21%)

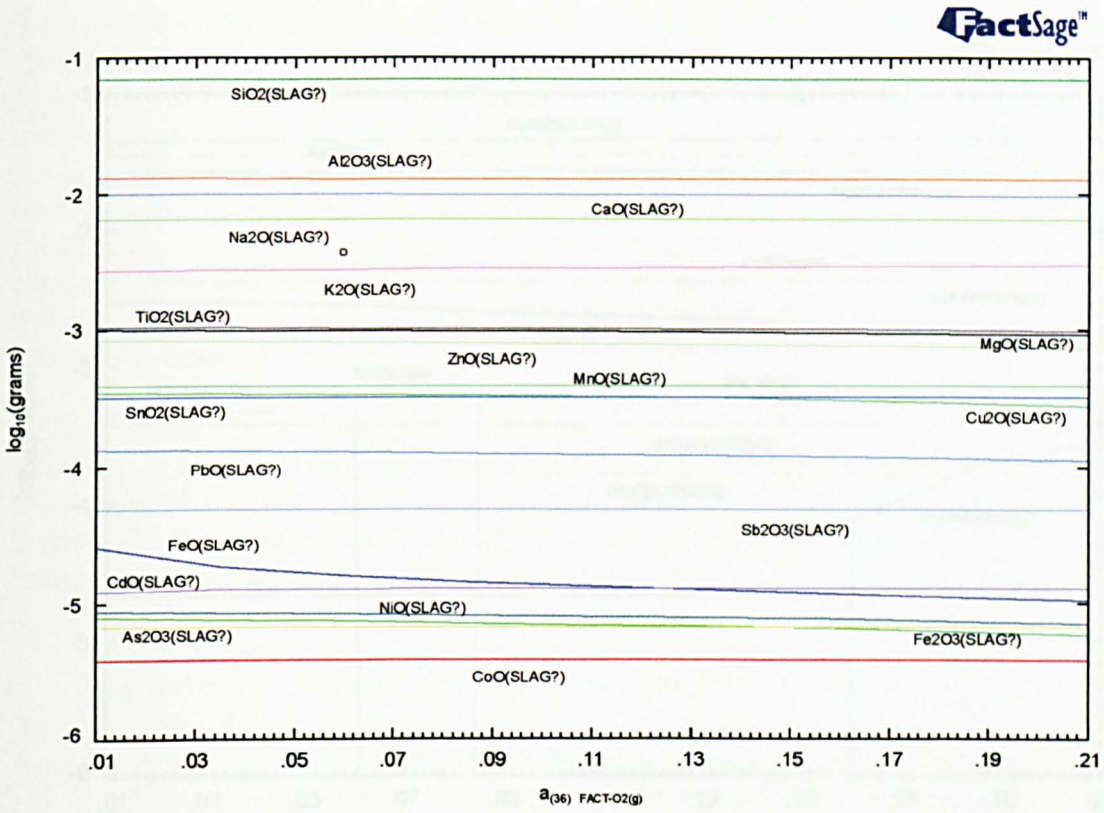


Figure 63: Major oxide slag components from MSW combustion with a range of oxygen concentrations (shown for oxygen activities between 0.01 and 0.21, i.e. 1-21%)

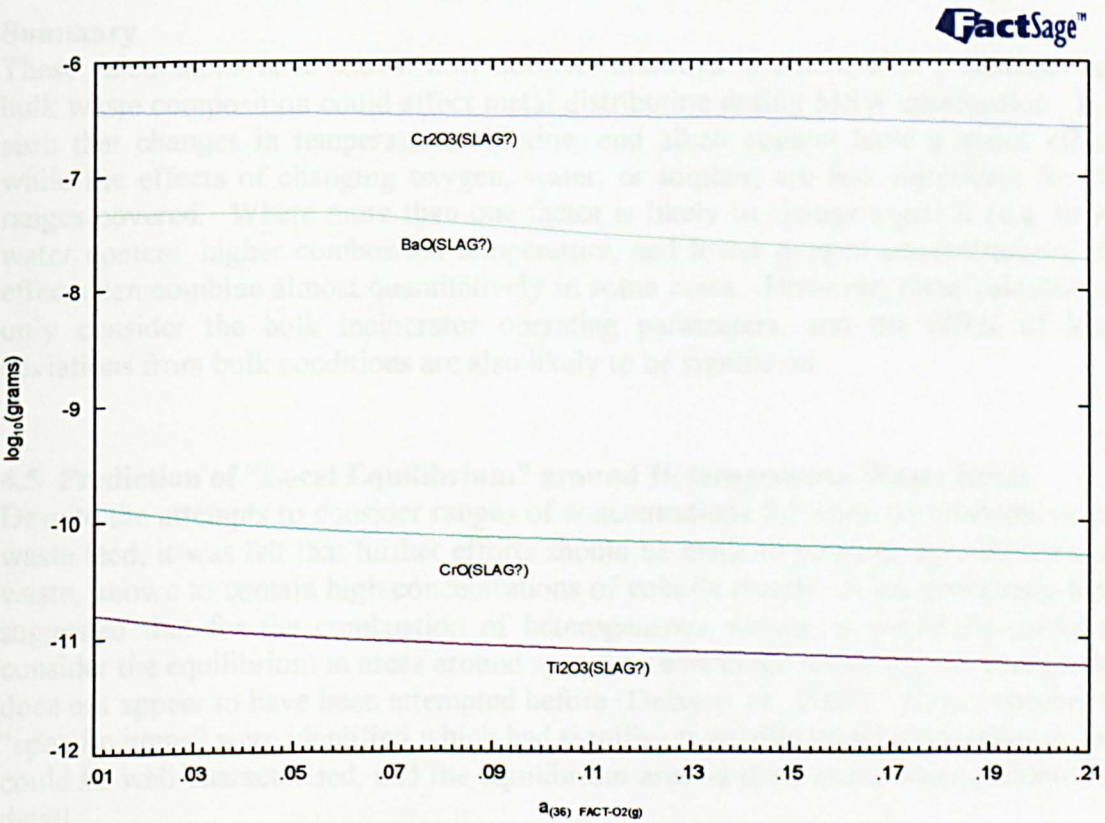


Figure 64: Minor oxide slag components from MSW combustion with a range of oxygen concentrations (shown for oxygen activities between 0.01 and 0.21, i.e. 1-21%)

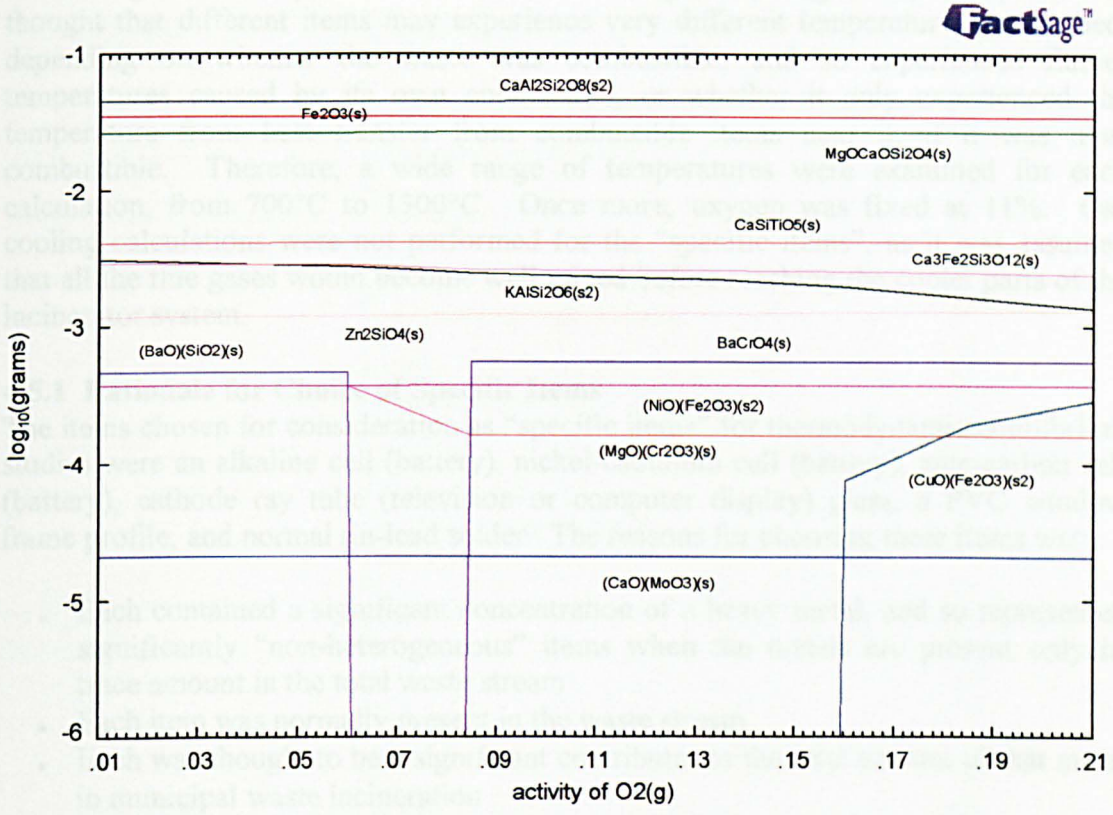


Figure 65: Pure solid components from MSW combustion with a range of oxygen concentrations (shown for oxygen activities between 0.01 and 0.21, i.e. 1-21%)

Summary

These calculations have shown how normal variations in combustion conditions and bulk waste composition could affect metal distribution during MSW combustion. It is seen that changes in temperature, chlorine, and alkali content have a major effect, while the effects of changing oxygen, water, or sulphur, are less significant for the ranges covered. Where more than one factor is likely to change together (e.g. lower water content, higher combustion temperature, and lower oxygen concentration), the effects can combine almost quantitatively in some cases. However, these calculations only consider the bulk incinerator operating parameters, and the effect of local deviations from bulk conditions are also likely to be significant.

4.5 Prediction of "Local Equilibrium" around Heterogeneous Waste Items

Despite the attempts to consider ranges of concentrations for some components of the waste feed, it was felt that further efforts should be made to consider specific items of waste, known to contain high concentrations of volatile metals. It has previously been suggested that for the combustion of heterogeneous wastes, it would be useful to consider the equilibrium in areas around specific items in the waste stream, though this does not appear to have been attempted before (Delay et al., 2001). Thus a number of "specific items" were identified which had significant volatile metal concentration, and could be well characterised, and the equilibrium around these items was considered in detail.

Determining the combustion temperature for such items was problematic. It is known that the temperature on the burning bed is extremely variable, and is not reflected in

the average bulk temperature of the incinerator gases (Yang et al., 2002). It was thought that different items may experience very different temperatures on the bed, depending on whether the waste was combustible, and so experienced flame-temperatures caused by its own combustion, or whether it only experienced the temperature from heat transfer from combustible items near it, if it was non-combustible. Therefore, a wide range of temperatures were examined for each calculation, from 700°C to 1300°C. Once more, oxygen was fixed at 11%. Gas cooling calculations were not performed for the "specific items", as it was assumed that all the flue gases would become well mixed before reaching the cooler parts of the incinerator system.

4.5.1 Rationale for Choice of Specific Items

The items chosen for consideration as "specific items" for thermodynamic equilibrium studies were an alkaline cell (battery), nickel-cadmium cell (battery), zinc-carbon cell (battery), cathode ray tube (television or computer display) glass, a PVC window frame profile, and normal tin-lead solder. The reasons for choosing these items were:

- Each contained a significant concentration of a heavy metal, and so represented significantly "non-heterogeneous" items when the metals are present only in trace amount in the total waste stream
- Each item was normally present in the waste stream
- Each was thought to be a significant contributor to the total amount of that metal in municipal waste incineration
- In addition to heavy metal (lead), the PVC contained chlorine, which promotes volatilisation (lead complexes are used as stabilisers in some PVC)
- These items could be well characterised from literature data
- The items displayed a range of ways of having metals present in the waste feed (from lead present as elemental metal in solder alloy, to as an organic compound, distributed at relatively low concentration in PVC products)
- The metals involved displayed partitioning behaviour in the incinerator which was not adequately explained by "bulk" equilibrium calculations alone

The elemental compositions of the items chosen, as found by literature search, are given in Table 44. Where the data from different sources were inconsistent or incomplete, an inference as to the overall composition of the item was made, using information from all the available sources.

Table 44: The composition of "specific waste items" used in thermodynamic modelling (wt %)

item & reference	component	percentage
alkaline cell/battery	carbon	10
(Duracell, 2004)	KOH	10
(Unyi, 1998)	MnO_2	30
(Monmouth, 2005)	steel casing (considered as Fe)	30
	Zn	20
nickel-cadmium cell/battery	Cd (metal)	26
(ChiefSupply.Com, 2004)	CdOH	26
(Monmouth, 2005)	Co	1
	KOH	3
	Ni	17
	NiOH	12
	nylon (insulation etc) $(C_{12}N_2H_{22}O_2)_n$	2
	steel casing (considered as Fe)	13
zinc-carbon cell/battery	carbon	10
(Monmouth, 2005)	Cl (present as $ZnCl_2$)	14
	Mn (presumed to be MnO_2)	38
	steel casing (considered as Fe)	8
	Zn	30
CRT glass	SiO_2	61.9
(ICER, 2005)	BaO	11.0
	Na_2O	9.0
	K_2O	7.0
	PbO	5.0
	SrO	2.0
	Al_2O_3	2.0
	CaO	0.7
	ZrO_2	0.4
	Sb_2O_3	0.3
	F	0.3
	CeO_2	0.1
	Fe_2O_3	0.2
	MgO	0.1
PVC window frame profile	$CaCO_3$ (filler)	6.3
(SpecialChem4Polymers.com,	TiO_2	5.9
2005)	stabiliser: $PbHPO_3.2PbO$	2.5
	stabiliser: $(C_{17}H_{35}COO)_2Pb$	1.1
	pure PVC polymer $(CH_2CHCl)_n$	84.2
tin-lead alloy solder*	Pb	40
(RS ltd, 2005)	Sn	60

* EC legislation now restricts use of tin-lead solder, but it is to be expected that it will be found in the waste stream for some time to come, as it has been the most common electronics solder for many years

4.5.2 Isolated Equilibrium Calculations

At first, some items were considered to be completely isolated from the bulk waste matrix around them. Simple equilibrium partitioning predictions were made at a relatively small number of temperatures using only the composition of the items themselves, and combustion air as the input components for the calculation. This presented a "limiting case" scenario, where the partitioning of metals in a specific waste item was entirely unaffected by the environment around it, apart from to heat the waste to combustion temperature.

However, it was felt that the results from such calculations would not be very realistic, as such items on the burning bed would be influenced by other waste burning around them. Attempts were therefore made to refine this modelling technique, having established that the results were indicating some interesting behaviours, which were significantly different from the calculations for general municipal waste.

4.5.3 Specific Items in the Combustion Gas Matrix

A second series of calculations were performed in which the "specific items" were considered to be surrounded by a gaseous atmosphere which was the product of the combustion of "typical municipal waste", as described above. This method sought to account for the fact that specific items would be surrounded by other combusting waste, which would produce a gaseous environment which may influence the partitioning within the specific items. For example, chlorine, which is present in many waste items may help to volatilise a metal in a non-chlorine containing product.

For this calculation, the FactSage™ programme was most helpful, as the gaseous products from one calculation could be used as part of the input for the next calculation. A simple calculation based on the waste composition data available indicated that the "specific items" were relatively uncommon in the waste stream, so the effect of one "specific item" on another was ignored. Thus 100g of the "specific item" was considered to be in equilibrium with 1kg of the flue gas from combustion of "typical waste", reflecting the relative abundance of such "specific items" (National Assembly for Wales, 2004, Belevi and Moench, 2000b). The composition of the bulk components of gas from "general waste combustion" is given in Table 45. In addition, further oxygen was supplied to maintain an overall oxygen level of 11% in the flue gas.

Table 45: The major component composition of flue gas, predicted by thermodynamic equilibrium calculation of "typical municipal waste" combustion

component	C	Cl	F	H	N	O	S
percentage	3.6	0.01	0.0002	0.08	74	22.2	0.002

The possible effect of liquid melts from the typical waste absorbing heavy metal from the specific items was ignored, as it was thought unlikely to happen in incinerator conditions. This is because it is thought that distances between items and melts on the bed would be too great for solid-liquid, liquid-liquid, or solid-solid contact, and it was assumed that only interactions of the specific item with the gas from waste combustion would be possible.

It should be emphasised that these calculations were not intended to give a full, quantitative description of the thermodynamic processes occurring on the burning bed. Rather, the intention was to demonstrate how non-equilibrium behaviour might influence metal partitioning. With the constraints of data availability, it would simply not be possible to consider all the "specific items" which might be present in waste separately, nor to assess fully how separate one "specific item" would be from the "general waste" matrix. Nevertheless, it was hoped that these calculations might indicate how "non-equilibrium" reactions, including local equilibria within the burning bed might contribute to the complexity which is known to exist in metal partitioning.

Thus a series of different thermodynamic predictions were used to try to rationalise the observed partitioning behaviour of volatile metals in combustion. The calculations sought to account for heterogeneity in the waste stream, and for variations in the combustion process, by considering a range of values for key parameters, and a number of important "specific items" in the waste stream. It was hoped that this information would help not only to explain existing partitioning data, but any data obtained on variation in metal volatilisation, as revealed by continuous monitoring.

4.5.4 Results: Prediction of "Local Equilibrium" around Specific Items

Isolated Equilibrium Calculations

Alkaline Cell (Battery)

The predicted composition of the products of "combustion" of a typical alkaline battery in 11% oxygen are shown in Table 46 for a range of temperatures. Compared with the predictions for "typical" waste, the results are much simpler, due to the smaller number of components considered. However, the results compare very interestingly with those for typical municipal waste, as they indicate that the volatilisation of both potassium and lead are much lower around the battery than in bulk conditions (typically <2%, compared with up to 100%), presumably due to the lack of halogen ions (and possibly the OH ion). Thus this example illustrates how inhomogeneous mixing on the burning bed could lead to local equilibrium conditions around specific items in the waste, leading to lower volatile metal evaporation than is conventionally expected. A slag melt is not predicted in the isolated equilibrium considered.

Table 46: The predicted percentage composition of products from combustion of an alkaline battery in complete isolation from any other waste (wt %)

element	predicted products	800°C	1050°C	1350°C	key specics
C	gas	53.92	53.92	54.64	CO2
	pure solid	46.08	46.08	45.36	K2CO3
K	gas	1.1E-09	1.2E-05	1.57	K, KO
	pure solid	100	100	98.43	K2CO3
N	gas	100	100	100	N2, NO
	pure solid	0	0	0	
O	gas	0.5925	0.5927	59.85	O2, CO2, NO, KO
	pure solid	0.4075	0.4073	40.15	
Zn	gas	2.9E-11	6.2E-07	0.16	Zn
	pure solid	100	100	99.84	ZnO

Nickel-Cadmium Cell (Battery)

The predicted composition of the products of "combustion" of a typical nickel-cadmium battery in 11% oxygen are shown in Table 47 for a range of temperatures. As with the alkaline battery, consideration of the nickel-cadmium cell leads to much lower predictions of evaporation of volatile metals than in the bulk MSW. This applies to cadmium, potassium, and nickel at lower temperatures, although at the higher temperatures, cadmium is predicted to volatilise completely in either situation.

Table 47: The predicted percentage composition of products from combustion of a nickel-cadmium battery in complete isolation from any other waste (wt %)

element	products predicted	800	1050	1350	key species
Cd	gas	0.00	0.96	100.00	Cd, CdO
	pure solid	100.00	99.04	0.00	CdO
K	gas	0.00	9.01	100.00	K, KO, K2
	pure solid	99.99	90.99	0.00	K2O2
N	gas	100.00	100.00	100.00	N2, NO
	pure solid	0.00	0.00	0.00	
Ni	gas	0.00	0.00	0.00	
	pure solid	100.00	100.00	100.00	NiO
O	gas	52.18	52.61	67.55	O2, CdO, NO, KO
	pure solid	47.82	47.39	32.45	NiO, CdO, K2O2

Zinc-Carbon Cell (Battery)

The predicted composition of the products of "combustion" of a typical zinc-carbon battery in 11% oxygen are shown in Table 48 for a range of temperatures. Once again, the small number of components means that the prediction results are simple. Manganese is seen to be slightly volatile, as $MnCl_2$, particularly at higher temperatures, more so than in typical municipal waste. Zinc is also seen to be more volatile in the isolated equilibrium than in typical municipal waste combustion, but the volatilisation (as $ZnCl_2$) is seen to be limited by chlorine availability (>90% of the Cl is present as ZnCl2), which means that the proportion of Zn volatilised alters little over the temperature range considered for the isolated equilibrium.

Table 48: The predicted percentage composition of products from combustion of a zinc-carbon battery in complete isolation from any other waste (wt %)

element	products predicted	800	1050	1350	key species
C	gas	100.00	100.00	100.00	CO2
Cl	gas	100.00	100.00	100.00	ZnCl2, MnCl2, Cl, Cl2
Mn	gas	1.88E-04	0.21	1.20	MnCl2
	pure solid	99.98	99.79	98.80	Mn2O3, Mn3O4
N	gas	100.00	100.00	100.00	N2, NO
O	gas	63.76	65.79	65.88	CO2, O2, NO
	pure solid	36.24	34.21	34.12	Mn2O3, Mn3O4, ZnO
Zn	gas	25.48	25.38	23.81	ZnCl2
	pure solid	74.52	74.62	76.19	ZnO

CRT Glass

The predicted composition of the products of "combustion" of typical CRT glass cullet in 11% oxygen are shown in Table 49 for a range of temperatures. Due to the unusual elemental composition of the item, several elements are included in the prediction which are not otherwise considered in the work on MSW incineration. Given that the item in question is a glass product, it is encouraging that the majority of the main components from the thermodynamic prediction are in the slag or gas phases, and not as pure species, indicating the successful modelling of the glass. In order to achieve this, the slag models used for this limited prediction are more complex than those used in predictions for full MSW incineration prediction, and account for chlorides and fluorides in the melt, as well as the oxides used in the main predictions. In the more extensive predictions, these models could not be used, due to lack of data availability for some elements, and the total complexity of the prediction involved. Compared with typical MSW, the volatilisation of aluminium is predicted to increase slightly,

through the formation of $OAlF_2$, while the volatilisation of slag-forming elements (notably Na and K) is reduced, due to the formation of a stable slag phase.

Table 49: The predicted percentage composition of products from combustion of mixed CRT glass in complete isolation from any other waste (wt %)

element	products predicted	800°C	1050°C	1350°C	key species
Al	gas	9.9E-07	2.4E-04	0.10	OAlF2
	Al in slag	100.00	99.98	99.90	Al2O3
Ba	gas	9.7E-09	2.1E-05	5.7E-04	BaF2
	pure solid	100.00	100.00	99.94	(BaO)(SiO2)
Ca	gas	1.1E-10	1.5E-07	2.3E-06	CaF2
	Ca in slag	63.53	100.00	100.00	CaO, CaF2
	pure solid	36.47	0.00	0.00	Na2CaSi5O12
Cl	gas	18.42	83.29	98.85	NaCl, KCl, PbCl, Cl, PbCl2, (NaCl)2, Cl, (KCl)2
	Cl in slag	81.58	16.71	1.15	NaCl, KCl, PbCl2, CaCl2, MgCl2
F	gas	0.65	82.37	94.26	NaF, KF, SiF4, PbF2, (NaF)2, BaF2, OAlF2, PbF, SrF2, ZrF4, (KF)2, OSiF2
	F in slag	13.04	17.63	5.74	NaF, KF, PbF2, CaF2, MgF2
	pure solid	86.32	0.00	0.00	BaF2
K	gas	2.0E-04	0.30	1.54	KF, KCl
	K in slag	99.98	99.70	98.46	K2O, KF, KCl
Mg	gas	1.7E-08	9.9E-06	9.4E-05	MgF2
	Mg in slag	100.00	100.00	99.99	MgO, MgF2, MgCl2
N	gas	100.00	100.00	100.00	N2, NO
Na	gas	7.8E-04	0.86	3.80	NaF, NaCl, (NaF)2, (NaCl)2
	Na in slag	96.93	99.14	96.20	Na2O, NaF, NaCl
	pure solid	2.99	0.00	0.00	Na2CaSi5O12
O	gas	18.02	18.21	18.60	O2, PbO, NO, Sb4O6
	O in slag	65.63	72.95	72.90	SiO2, Na2O, K2O, Al2O3, PbO, CaO, ZrO2, MgO
	pure solid	16.35	8.84	8.50	(BaO)(SiO2), (SrO)(SiO2), ZrO2, ZrSiO4
Pb	gas	0.57	3.15	31.76	PbO, PbF2, PbF, Pb, PbCl, PbCl2
	Pb in slag	99.43	96.85	68.24	PbO, PbF2
Sb	gas	9.7E-04	100.00	100.00	Sb4O6
	pure solid	99.90	0.00	0.00	SbO2
Si	gas	1.80E-05	0.24	3.81E-04	SiF4
	Si in slag	81.10	91.36	91.83	SiO2
	pure solid	18.90	8.41	8.14	(BaO)(SiO2), (SrO)(SiO2)
Sr	gas	3.7E-10	1.9E-06	1.4E-04	SrF2
	pure solid	100.00	100.00	99.99	(SrO)(SiO2)
Zr	gas	3.85E-08	1.60E-04	4.44E-04	ZrF4(g)
	Zr in slag	0.18	4.91	73.23	ZrO2
	pure solid	99.82	95.08	26.73	ZrSiO4, ZrO2

Overview of Information Obtained from Study of Isolated Local Equilibrium

These simple initial calculations of thermodynamic equilibrium around specific heterogeneous items indicate how local equilibrium conditions can differ substantially from bulk equilibrium, significantly altering metal volatilisation. Where slag formation occurs, this tends to reduce volatilisation, as does lower availability of halogens, and possibly water. In contrast, increased halogen concentration can lead to enhanced volatilisation of some metals in isolated equilibria.

However, despite providing useful "limiting case" scenarios for the combustion of specific items in the waste stream, the complete exclusion of the surrounding combustion matrix appears to be a significant simplification. Further, more detailed calculations were therefore completed (for a larger number of combustion temperatures) where the matrix was accounted for, with 100g of the "specific item" being in equilibrium with 1000g of typical municipal waste combustion gas.

Specific Items in Combustion Gas Matrix

Alkaline Cell (Battery)

The predicted composition of the products of "combustion" of a typical alkaline battery in typical MSW flue gas (as predicted in earlier calculations) are shown in Table 50 for a range of temperatures. Once more, these results compare interestingly with those for typical MSW, and also for those for the battery in complete isolation. In the flue gas matrix, the volatilisation of potassium is predicted to be slightly higher at all temperatures in the equilibrium around the battery than in the bulk waste. This is in contrast to the battery in complete isolation, and illustrates the effect of halogens (and OH) in the bulk flue gases in enhancing the volatility of the volatile metals in a specific item in the waste stream. Interestingly, a stable solid sulphate of potassium is also predicted, whereas a potassium oxide slag component is predicted in typical MSW combustion, thus suggesting that slag formation may be retarding volatility. In contrast, the volatility of zinc is suppressed, when compared with predictions for "typical" MSW, presumably due to the competition between zinc and potassium for the limited amount of available chlorine, and the availability of a stable zinc-iron solid compound. The volatility of manganese is also suppressed (it is predicted to volatilise a very small amount in typical MSW, and not significantly at all in the battery equilibrium).

Table 50: The predicted percentage composition of products from combustion of an alkaline battery in the flue gas matrix from "typical MSW" combustion (wt %)

element	predicted products	700°C	850°C	950°C	1050°C	1300°C	key species
C	gas	97.75	97.77	97.93	98.79	100.00	CO2
	pure solid	2.25	2.23	2.07	1.21	0.00	K2CO3
Cl	gas	100.00	100.00	100.00	100.00	100.00	KCl, (KCl)2, HCl
	pure solid	0.00	0.00	0.00	0.00	0.00	
F	gas	100.00	100.00	100.00	100.00	100.00	KF, HF, (KF)2
	pure solid	0.00	0.00	0.00	0.00	0.00	
Fe	gas	0.00	0.00	0.00	0.00	0.00	Fe(OH)2
	pure solid	100.00	100.00	100.00	100.00	100.00	ZnFe2O4 (lower temps), (MnO)(Fe2O3) (higher temps)
H	gas	100.00	100.00	100.00	100.00	100.00	H2O, KOH, OH, (KOH)2
	pure solid	0.00	0.00	0.00	0.00	0.00	
K	gas	1.65	2.57	9.42	47.03	100.00	KOH, KCl, (KCl)2 K, K2SO4, KO, KF, (KOH)2
	pure solid	98.35	97.43	90.59	52.97	0.00	K2CO3, K2SO4
Mn	gas	0.00	0.00	0.00	0.00	0.00	MnCl2, Mn
	pure solid	100.00	100.00	100.00	100.00	100.00	Mn3O4 (lower temps), (MnO)(Fe2O3) (higher temps)
N	gas	100.00	100.00	100.00	100.00	100.00	N2, NO
	pure solid	0.00	0.00	0.00	0.00	0.00	
O	gas	89.22	89.53	89.64	90.22	91.54	CO2, O2, H2O, KOH, NO
	pure solid	10.78	10.47	10.36	9.78	8.46	ZnFe2O4 (lower temps), (MnO)(Fe2O3) (higher temps), ZnO, Mn3O4
S	gas	2.28E-05	0.36	4.91	43.50	100.00	K2SO4
	pure solid	100.00	99.64	95.09	56.50	0.00	K2SO4
Zn	gas	0.00	0.00	0.00	0.00	0.38	ZnCl2, Zn
	pure solid	100.00	100.00	100.00	100.00	99.62	ZnFe2O4, ZnO

Nickel-Cadmium Cell (Battery)

The predicted composition of the products of "combustion" of a typical nickel-cadmium battery in typical MSW flue gas are shown in Table 51for a range of temperatures. Although predicted volatility of cadmium is higher than for the isolated Ni-Cd equilibrium, it is still lower than for cadmium in "typical" municipal waste. The volatility of the trace amounts of cobalt (found as an impurity in nickel) is suppressed in the equilibrium around the battery. In contrast to these, the volatility of potassium is higher in the equilibrium around the battery than in municipal waste combustion, presumably mainly because of the lack of availability of a stabilising potassium slag phase in the local equilibrium. The presence of chlorine also increases potassium volatility, compared with volatilisation of potassium from the completely isolated battery.

Table 51: The predicted percentage composition of products from combustion of a nickel-cadmium battery in the flue gas matrix from "typical MSW" combustion (wt %)

element		700°C	850°C	950°C	1050°C	1300°C	key species
C	gas	99.22	99.25	99.50	100.0	100.0	CO2, CO
	pure solid	0.7830	0.7497	0.4996	0.0000	0.0000	K2CO3
Cd	gas	0.00	0.03	0.3879	4.429	100.0	Cd, CdO, Cd(OH)2, CdOH
	pure solid	100.0	99.97	99.61	95.57	0.00	CdO
Cl	gas	100.0	100.0	100.0	100.0	100.0	KCl, HCl, (KCl)2, Cl
Co	gas	0.00	0.00	0.00	0.00	0.00	Co
	pure solid	100.0	100.0	100.0	100.0	100.0	(CoO)(Fe2O3)
F	gas	100.0	100.0	100.0	100.0	100.0	KF, HF, (KF)2
Fe	gas	0.00	0.00	0.00	0.00	0.00	Fe(OH)2
	pure solid	100.0	100.0	100.0	100.0	100.0	(NiO)(Fe2O3), (CoO)(Fe2O3)
H	gas	100.0	100.0	100.0	100.0	100.0	H2O, KOH, OH, Cd(OH)2, CdOH, Ni(OH)2, H2, HF, HOO, (KOH)2, HCl
K	gas	5.508	9.424	38.87	98.47	100.0	KOH, KCl, K2SO4, K, KO, (KOH)2, (KCl)2, KF, (KF)2
	pure solid	94.49	90.58	61.13	1.533	0.0000	K2CO3, K2SO4
N	gas	100.0	100.0	100.0	100.0	100.0	N2, NO, NO2
Ni	gas	0.00	0.00	0.00	0.00	0.00	Ni(OH)2
	pure solid	100.0	100.0	100.0	100.0	100.0	NiO, (NiO)(Fe2O3)
O	gas	91.61	91.63	91.79	92.21	94.77	O2, CO2, H2O, CdO, KOH, NO, K2SO4, OH, Cd(OH)2, SO2, NO2, CO, O, CdOH, Ni(OH)2, KO, (KOH)2
	pure solid	8.393	8.371	8.207	7.788	5.232	(NiO)(Fe2O3), NiO, (CoO)(Fe2O3), CdO, K2CO3, K2SO4
S	gas	0.00	0.3514	4.839	42.87	100.0	K2SO4, SO2, SO3
	pure solid	100.0	99.65	95.16	57.13	0.0000	K2SO4

Zinc-Carbon Cell (Battery)

The predicted composition of the products of "combustion" of a typical zinc-carbon battery in typical MSW flue gas are shown in Table 52 for a range of temperatures. The predictions are very similar to those for the zinc carbon battery in isolation, with slightly increased volatilisation of zinc and manganese, presumably due to the extra chlorine available from the flue gas matrix. Again, metal volatilisation is significantly increased over predictions for typical MSW.

Table 52: The predicted percentage composition of products from combustion of a zinc-carbon battery in the flue gas matrix from "typical MSW" combustion (wt %)

element	predicted products	700°C	850°C	950°C	1050°C	1300°C	key species
C	gas	100.0	100.0	100.0	100.0	100.0	CO2, CO
Cl	gas	100.0	100.0	100.0	100.0	100.0	ZnCl2, HCl, MnCl2, Cl, FeCl2, Cl2, ClO, HOCl, FeCl3, ONCl
F	gas	100.0	100.0	100.0	100.0	100.0	HF, F
Fe	gas	2.3E-04	1.3E-03	1.9E-02	1.9E-02	0.2185	FeCl2, FeCl3
	pure solid	100.0	100.0	99.98	99.98	99.78	ZnFe2O4 (low temps), (MnO)(Fe2O3) (high temps)
H	gas	100.0	100.0	100.0	100.0	100.0	H2O, HCl, OH, HF, H2, HOCL, HOO, Fe(OH)2
Mn	gas	5.3E-03	4.5E-02	0.2827	0.2827	1.298	MnCl2
	pure solid	99.99	99.95	99.72	99.72	98.70	Mn2O3 (low temps), Mn3O4, (MnO)(Fe2O3) (high temps)
N	gas	100.0	100.0	100.0	100.0	100.0	N2, NO, NO2
	gas	90.93	91.59	91.63	91.63	91.81	CO2, O2, H2O, NO, OH, SO2, NO2, CO, O, ClO, SO3
	pure solid	9.065	8.406	8.368	8.368	8.189	Mn3O4, ZnO, (MnO)(Fe2O3), Mn2O3, ZnFe2O4
S	gas	100.0	100.0	100.0	100.0	100.0	SO2, SO3, SO
Zn	gas	30.86	32.65	33.41	33.41	32.54	ZnCl2, Zn
	pure solid	69.14	67.35	66.59	66.59	67.46	ZnO, ZnFe2O4

CRT Glass

The predicted composition of the products of "combustion" of CRT glass cullet in typical MSW flue gas are shown in Table 53 for a range of temperatures. Predictions are not shown for the usual lowest temperature of 700°C as slag formation does not begin at such a low temperature. The enhanced slag models, used in the isolated CRT glass prediction, could not be used, due to the increased number of species introduced by the inclusion of flue gas from normal MSW combustion in the calculation, and the added complexity introduced by doing so. Despite this simplification, the prediction of slag formation remains good. The predictions show volatile elements, such as Na, K, and Pb, which are involved in slag formation, have lower volatility than in normal MSW, due to the stable slag formation.

Table 53: The predicted percentage composition of products from combustion of CRT glass cullet in the flue gas matrix from "typical MSW" combustion (wt %)

element	predicted products	850°C	950°C	1050°C	1300°C	key species
Al	gas	2.9E-05	6.4E-05	1.2-04	2.5E-04	OAlF2
	Al in slag	100.0	100.0	100.0	100.0	Al2O3
Ba	gas	6.8E-07	2.2E-06	7.2E-06	9.2E-05	BaF2
	Ba in slag	3.4E-06	2.5E-05	1.3E-04	3.2E-03	BaO
	pure solid	100.0	100.0	100.0	100.0	(BaO)(SiO2)
C	gas	100.0	100.0	100.0	100.0	CO2, CO
Ca	gas	5.3E-09	1.7E-08	5.3E-08	4.2E-07	CaF2
	Ca in slag	100.0	100.0	100.0	100.0	CaO
Ce	gas	9.8E-18	1.2E-15	6.8E-14	1.9E-10	CeO3H3
	Ce in slag	4.6E-07	2.4E-05	6.9E-04	0.47	Ce2O3
	pure solid	100.0	100.0	100.0	99.53	CeO2
Cl	gas	100.0	100.0	100.0	100.0	NaCl, KCl, HCl, Cl, PbCl, (NaCl)2, PbCl2, ClO, HOCl, (KCl)2, FeCl2
F	gas	100.0	100.0	100.0	4.0492 E-17	HF, NaF, KF, PbF, (NaF)2, PbF2, OAlF2, FeF3, BaF2, F
Fe	gas	1.5E-03	1.9E-03	2.6E-03	4.3E-02	Fe(OH)2, FeF3, FeO
	Fe in slag	0.1715	0.7514	3.353	99.96	FeO, Fe2O3
	pure solid	99.83	99.25	96.64	0.0000	Fe2O3
H	gas	100.0	100.0	100.0	100.0	H2O, HF, OH, NaOH, HCl, KOH, H2, HOO, Fe(OH)2
K	gas	0.1287	0.2087	0.2734	0.4999	KCl, KF, KOH, K, (KCl)2, K2SO4
	K in slag	99.87	99.79	99.73	99.50	K2O
Mg	gas	5.2E-07	1.5E-06	3.8E-06	2.2E-05	MgF2
	Mg in slag	100.0	100.0	100.0	100.0	MgO
N	gas	100.0	100.0	100.0	100.0	N2, NO, NO2
Na	gas	0.4423	0.6255	0.7551	1.334	NaCl, NaF, NaOH, Na, (NaF)2, NaO, Na2SO4, (NaCl)2
	Na in slag	99.09	99.37	99.24	98.67	Na2O
	pure solid	0.4722	0.00	0.00	0.00	Na2SO4
O	gas	84.82	84.84	84.86	85.00	O2, CO2, H2O, NO, PbO, OH, SO2, NaOH, NO2, CO, O, KOH, SO3
	O in slag	13.39	13.38	13.36	13.31	SiO2, Na2O, K2O, Al2O3, CaO, PbO, ZrO2, Sb2O3, MgO, FeO, Fe2O3
	pure solid	1.796	1.778	1.774	1.691	(BaO)(SiO2), (SrO)(SiO2), ZrO2, CeO2
Pb	gas	1.032	2.850	13.10	79.65	PbO, Pb, PbCl, PbF, PbF, PbCl2
	Pb in slag	98.97	97.15	86.90	20.35	PbO
S	gas	4.400	100.0	100.0	100.0	SO2, SO3, Na2SO4, K2SO4, SO
	pure solid	95.60	0.00	0.00	0.00	
Sb	gas	4.4E-02	4.7E-02	4.8E-02	4.9E-02	Sb4O6, (SbO2H2)
	Sb in slag	99.96	99.95	99.95	99.95	Sb2O3
Si	gas	1.1E-06	3.8E-07	1.6E-07	2.2E-07	OSiF2, SiF4
	Si in slag	90.85	90.85	90.86	91.16	SiO2
	pure solid	9.151	9.148	9.137	8.837	(BaO)(SiO2), (SrO)(SiO2), ZrSiO4
Sr	gas	7.6E-08	2.5E-07	9.0E-07	2.4E-05	SrF2, SrCl2
	pure solid	100.0	100.0	100.0	100.0	(SrO)(SiO2)
Zr	gas	5.0E-09	7.8E-09	1.1E-08	1.6E-08	ZrF4(g)
	Zr in slag	0.3800	1.528	4.987	51.73	ZrO2
	pure solid	99.62	98.47	95.01	48.27	ZrO2, ZrSiO4

PVC window frame profile

The predicted composition of the products of combustion of a lead stabiliser-containing PVC product in typical MSW flue gas are shown in Table 54 for a range of temperatures. In this situation, all of the lead is volatilised at all temperatures, as there

is no stabilisation by slag formation. In addition, the example shows how a local equilibrium could lead to calcium volatilisation, which is not conventionally expected.

Table 54: The predicted percentage composition of products from combustion of a PVC window profile in the flue gas matrix from "typical MSW" combustion (wt %)

element	predicted products	700°C	850°C	950°C	1050°C	1300°C	key species
C	gas	100.0	100.0	100.0	100.0	100.0	CO2, CO
Ca	gas	3.1E-04	4.1E-02	0.4662	3.547	100.0	CaCl2, Ca(OH)2
	pure solid	100.0	99.96	99.53	96.45	0.00	CaCl2, CaSO4
Cl	gas	86.30	86.30	86.28	86.34	100.0	HCl, CaCl2, Cl, PbCl2, Cl2, ClO, PbCl, HOCl, ONCl, PbCl4
	pure solid	13.70	13.70	13.72	13.66	0.00	
F	gas	100.0	100.0	100.0	100.0	100.0	HF, F
H	gas	100.0	100.0	100.0	100.0	100.0	H2O, HCl, OH, HOCl, HF, H2, HOO
N	gas	100.0	100.0	100.0	100.0	100.0	N2, NO, NO2
O	gas	99.94	99.94	99.95	100.0	100.0	CO2, O2, H2O, NO, SO2, OH, ClO, NO2, CO, O, HOCl, PbO, SO3, HOO
	pure solid	5.8E-02	5.7E-02	4.6E-02	0.00	0.00	
Pb	gas	100.0	100.0	100.0	100.0	100.0	PbCl2, PbCl, PbO, Pb, PbCl4
S	gas	1.7E-02	1.500	19.71	100.0	100.0	SO2, SO3, SO
	pure solid	99.98	98.50	80.29	0.00	0.00	CaSO4

Conventional tin-lead solder

The predicted composition of the products of "combustion" of conventional tin-lead solder in typical MSW flue gas are shown in Table 55 for a range of temperatures. Unlike the prediction for "typical" waste, where lead is predicted to be volatile at all temperatures, the effect of local equilibrium is to suppress lead volatility, with a significant proportion of the lead in solder being predicted to remain in solid phase at the lower combustion temperatures. At higher temperatures, once more lead is predicted to volatilise completely. As with "typical" waste combustion, tin in solder is not predicted to be volatile in MSW incineration conditions.

Table 55: The predicted percentage composition of products from combustion from tin-lead solder in the flue gas matrix from "typical MSW" combustion (wt %)

element	products predicted	700°C	850°C	950°C	1050°C	1300°C	key species
C	gas	100.0	100.0	100.0	100.0	100.0	CO2, CO
Cl	gas	100.0	100.0	100.0	100.0	100.0	HCl, PbCl, PbCl2, Cl, ClO, HOCl, Cl2, ONCl, SnCl2
F	gas	100.0	100.0	100.0	100.0	100.0	HF, PbF, PbF2, F
H	gas	100.0	100.0	100.0	100.0	100.0	H2O, HCl, OH, HF, H2, HOO
N	gas	100.0	100.0	100.0	100.0	100.0	N2, NO, NO2
O	gas	92.01	92.04	92.28	93.32	93.34	O2, CO2, H2O, PbO, NO, OH, SO2, NO2, CO, O, SnO, SnO2, SO3
	pure solid	7.989	7.960	7.724	6.677	6.659	SnO2, PbO, (PbO)4(PbSO4)
Pb	gas	0.6900	2.807	20.06	100.0	100.0	PbO, PbCl, Pb, PbCl2
	pure solid	99.31	97.19	79.94	0.00	0.00	
S	gas	4.0E-03	2.059	61.59	100.0	100.0	SO2, SO3, SO
	pure solid	100.0	97.94	38.41	0.00	0.000	(PbO)4(PbSO4)
Sn	gas	3.7E-12	1.9E-09	1.4E-07	6.8E-06	1.9E-02	SnO, SnO2, (SnO2H2)
	pure solid	100.0	100.0	100.0	100.0	99.98	SnO2

Overview of Information Obtained from Study of Local Equilibrium

Thus it is seen how local equilibria around inhomogeneous items on the burning bed can significantly vary from the bulk equilibrium, affecting the volatility of some metals. In some cases, volatility is enhanced, providing explanations for how some "non-volatile" metals may be found in the flue gases or APC residue, and in other cases volatility is suppressed, explaining how volatilisation is not as complete in some situations as is predicted by bulk calculations. The results of calculations where the surrounding gas matrix is included can differ significantly from those for completely isolated specific item calculations, illustrating the importance of understanding the extent of interactions between different items on the burning bed, and the extent of inhomogeneity encountered.

4.6 Summary of use of Thermodynamic Calculations to Predict Metal Volatility

State-of-the-art thermodynamic calculations have been used to predict the equilibrium composition of the products from incineration. One calculation has considered the equilibrium for typical municipal waste combustion at a range of combustion temperatures, and for cooling of the combustion gas. A series of calculations has examined the effect of changing waste composition on equilibrium products. Further calculations of "local equilibrium" around specific metal-containing items in the waste stream have illustrated how non-uniformity on the burning bed could lead to unusual "local equilibrium" metal distributions. Such behaviour can vary significantly from the average on the entire burning bed, and show how routes may become available for enhanced or suppressed volatility for specific metals. The various calculations have served to illustrate how complex the equilibrium on the burning bed may be, and how unusual behaviour in terms of metal emission may be linked to specific items on the bed, or specific combustion conditions or overall waste composition.

Chapter Five:

Results

Information has been obtained from various sources on the partitioning of metals during municipal solid waste incineration. Temporal changes in metal volatilisation have been measured directly, through on-line monitoring of metal concentrations in cleaned and un-cleaned flue gases. Concentrations of metals in incinerator residues have been measured through digestion and analysis of the solids. Indicative data on the volatilisation of different metals and metal compounds in incinerator conditions, including species formed in the furnace, have been studied in the laboratory. Thus a comprehensive picture has been established experimentally of how different metals behave in the furnace environment. Combined with theoretical predictions made in Chapter 4, a unique insight is obtained into how metals behave during waste incineration.

5.1 Use of the CEML to Investigate the Behaviour of Metals in Combustion Systems

The CEML was used to detect vaporisation of metals and metal compounds in a combustion system, using the laboratory furnace described in Chapter 3. These screening experiments served both to check that metals could be detected in a real combustion system using the CEML, and to test preliminary theories about metal volatilisation using a series of different metals and metal compounds. It was also seen that non-volatile metals could react in the furnace to form volatile species, which were subsequently volatilised, indicating that reactions occurring on the burning bed may be significant to metal volatilisation.

5.1.1 Volatilisation of Various Metals and Metal Compounds

Numerous metals and metal compounds were tested for their volatility in the test furnace. According to the data obtained from the literature review (Chapter 2), some of these species were expected to be volatile, while others were not. The data obtained from these laboratory experiments are summarised in Table 56. It must be emphasised that the reactions shown are not supposed to be an exhaustive list of all the possible volatilisation routes possible, but are merely indicative of the sort of compounds which may lead to metal volatilisation in the furnace, adding to the information already available on volatility, reviewed in Chapter 2.

Table 56: Summary of results obtained for metal volatilisation studies

species	mass	boiling point (°C) (Weast et al., 1988)	metal seen in gas	comments
Al	0.8g	2467	no	as expected
Al_2O_3	1.0g	2980	no	as expected
Ca	0.6g	1484	no	as expected
Cr	0.7g	2672	no	as expected
Cu	0.5g	2567	no	as expected
$CuCl_2$	0.2g	993*	yes	slow release seen over several minutes
CuCl	0.2g	1490	yes	more clearly resolved peak seen
Fe	0.2g	2750	no	principal component of probe etc is iron, but iron not normally seen during experimental runs
$FeCl_2$	0.2g	NA	no	some Fe seen due to furnace flue corrosion
KOH	0.2g	1320	yes	very little seen, not really expected in significant quantity, and most of material was not volatilised
Mg	0.5g	1107	yes	not really expected, but seen (presumed to be entrained, Mg powder was used for this experiment)
NaOH	0.2g	1390	no	as expected
Ni	0.9g	2730	no	as expected
$NiCl_2$	0.2g	973*	no	not detected
Pb	2g	1740	no	not detected
$PbCl_2$	0.2g	950	yes	significant delay seen between addition and volatilisation temperature being reached
Sn	0.6g	2260	no	as expected
$SnCl_2$	0.2g	652	yes	as expected
Zn	0.7	907	no	not detected
$ZnSO_4$	0.2g	600*	yes	relatively minor peak, due to decomposition of sulphate?
$ZnCl_2$	0.3g	732	yes	as expected

A typical measured metal emission profiles for an individual experiment is shown in Figure 66. This type of result is typical for the furnace volatilisation experiments, and demonstrates that copper (II) chloride is slightly volatile, being released slowly over several minutes, whereas copper (I) chloride is much more volatile, being released rapidly, and leading to a significant emission peak, which lasts about 3 minutes. This is in contrast to the addition of copper metal to the furnace, which resulted in no measurable copper emission in the flue gas.

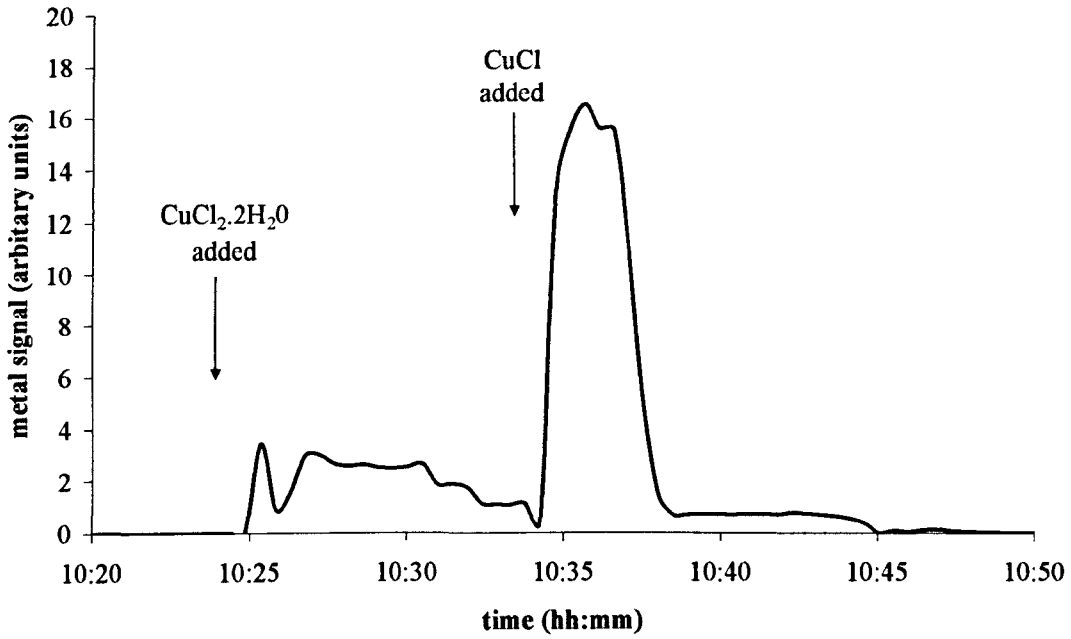


Figure 66: The emissions of copper from a laboratory furnace spiked with copper (I) and copper (II) chloride, as measured on the Cu I 324.754 nm emission wavelength

Thus with a series of simple furnace spiking experiments, it was seen that various metal salts could be volatilised in a laboratory furnace, and detected using the CEML. Depending on the material concerned, sometimes the volatilisation was complete, i.e. no solid residue remained (e.g. for mercury, seen in Chapter 3), whereas with others the volatile product was minor, with the majority of the reaction products being solid residues (e.g. for KOH). The results were largely as expected from the existing information on metal volatilisation, though it was found that even in these simple experiments, volatilisation is not straightforward. The emission spike shape and delay after the introduction to the furnace depended on the volatilisation rate, the thermal transfer in the furnace, the volatility of the metal salt concerned, and possibly reactions which lead to non-volatile products. Thus it was inferred that reactivity and kinetics could be important in metal volatilisation, and further studies were made to determine whether reactions in the furnace could also lead to further metal volatilisation. This is the subject of the following section (5.1.2).

5.1.2 Volatile Products from Reactions of Metals in the Combustion System

It has been explained in the literature review (Chapter 2) that the burning bed of an incinerator is a complex reacting system, and that reactions of metals or metal compounds with other species on the burning bed may enhance or suppress volatility. Using the laboratory furnace to provide a combustion environment, and the CEML to monitor gaseous products, studies were conducted into whether reactions could occur between different species on the bed, which would increase or decrease the volatility of certain metal. Again the list of experiments is not exhaustive, but serves to illustrate the sort of reactions which may be important in affecting metal partitioning. In a typical experiment, a non-volatile metal, such as lead or zinc, was placed in the furnace with a compound which could provide an anion, such as chloride. If the metal and anion reacted to produce a volatile product, this was seen in the furnace exhaust. The purposes of individual experiments, and anticipated products were given in Chapter 3, and an overview of the results is given in Table 57.

Table 57: Reactants added to the laboratory furnace to assess burning-bed volatilisation reactions

species 1	species 2	volatile products seen?	comments
Sn	$HONH_3Cl$	yes	non-metallic source of HCl, presumed to produce $SnCl_2$
Sn	NH_4I	yes	source of HI, presumed to form SnI_2
Sn	I_2	yes	source of I_2 presumed to form SnI_2
Sn	S	no	Either Sn does not react, or SnS forms
Sn	PVC	yes	"real" source of HCl in waste, presumed to form $SnCl_2$
Sn	PVC + S	yes	Although volatile product is seen, relative magnitude of peak is less, suggesting competing reaction with S to form non-volatile product
Pb	$HONH_3Cl$	yes	non-metallic source of HCl yields volatile lead compound, presumably $PbCl_2$
Pb	$ZnCl_2$	yes	both Zn and Pb volatilised
Pb	$SnCl_2$	yes	Both Sn and Pb volatilised, and some residual Zn
Pb	$NiCl_2$	yes	Pb (only) volatilised
Pb	$CuCl_2$	yes	Pb volatilised, with a trace of Cu
Al	$HONH_3Cl$	no	some residual Pb volatilised
Al	$ZnCl_2$	yes	both Zn and Al volatilised
Al	$SnCl_2$	yes	no Al volatilised. Mixture of Sn and residual Pb found in flue gas
Al	$NiCl_2$	no	no significant volatilisation
Al	$CuCl_2$	yes	significant quantities of Cu released, more than in the absence of Al
Zn	$HONH_3Cl$	yes	significant volatilisation of Zn (presumed to be as $ZnCl_2$), residual Pb also volatilised
Zn	$SnCl_2$	yes	Zn is major volatile product, some Sn and residual Pb
Zn	$NiCl_2$	Yes	Zn is major volatile product, some residual Pb
Zn	$CuCl_2$	Yes	Zn is major volatile product, some Cu, residual Pb
Zn	$PbCl_2$	yes	Zn is major volatile product, some Pb

A typical emission profile for a series of furnace reactions is shown in Figure 67. This experiment studied the volatilisation of tin, and it shows that while tin itself is not volatile (hence no tin is seen in the flue gas when tin metal is added to the furnace), tin can react with various halogen sources in the furnace to produce volatile tin products, but that these reactions can be inhibited by sulphur, which does not itself react with tin to form volatile products. It is also shown that waste PVC can act as a suitable source of chlorine for metal volatilisation. Thus the complexity of reaction which may be occurring on the burning bed of a municipal waste incinerator is illustrated, where all these compounds, and far more besides, may be reacting, forming volatile or non-volatile products.

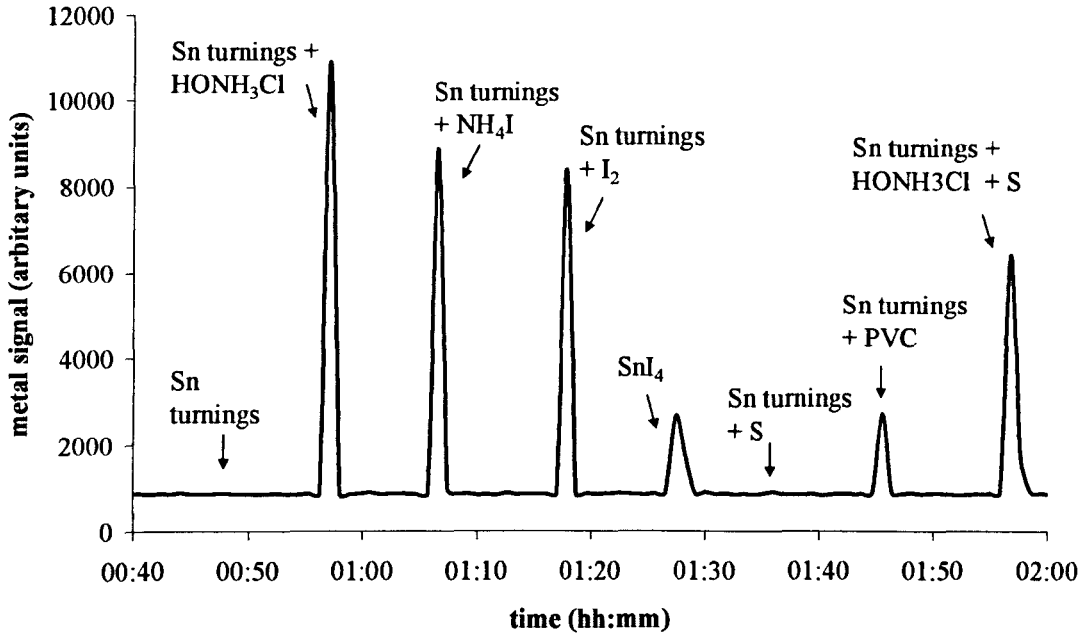


Figure 67: The release of tin in the furnace exhaust following various spiking experiments

Summary

Thus it is seen, from a range of relatively simple experiments, in which solid reagents volatilise or react and volatilise in a furnace environment, that the gaseous products measured using the CEML reveal a complex reaction system. It is seen that reactions can occur in the furnace, promoting or inhibiting the volatility of different metals, and that different metal compounds can interact with one another. The experiments illustrate the range and complexity of reactions which may occur on the burning bed to enhance (or inhibit) metal volatility, but are not intended to be an exhaustive or quantitative study of the factors involved. Thus full calibration of the analytical system was not always required. Instead, the aim was quickly to establish a range of elements and compounds which may be significant in metal volatilisation, and also to establish the success of the CEML in detecting various metals in the flue gas. Where these experiments have also yielded significant information on the volatilisation of particular metals, supporting the thermodynamic predictions made, and the results from experimentation at a municipal solid waste incineration plant, these are referred to in Chapter 6 where the overall findings are summarised for each metal studied.

The experiments indicate that the volatilisation of one metal is dependent on the anions available and other metals present, which may or may not be volatilised themselves. Given the complexity of the system, as demonstrated by the reactions shown, it was determined that the best way to discover more about metal concentrations in the flue gas from municipal waste was to measure them directly, on-site, with the use of the CEML. Nevertheless, these experiments have shown which species may be important in the volatilisation of different metals, which helps to support the findings of the on-site experimentation, along with the thermodynamic predictions of volatility.

5.2 Analysis of solids from a Municipal Solid Waste Incinerator

Two experimental studies were conducted at an industrial municipal solid waste incinerator, which was operating under normal conditions during measurements. The

main focus of these studies was on-line measurements of metal concentrations in flue gas using the CEML. During both studies, and during another site visit, confirmatory samples of solid residues were sampled, to provide further information on the metal concentrations in the system being studied. The results of these analyses are given below.

Samples collected during on-site experimentation were dissolved in a mixture of strong mineral acids (nitric and hydrochloric acid), and analysed for most metals by ICP-OES. Silicates and aluminosilicates were not fully dissolved, so the analysis for silicon cannot be given, and the values indicated for aluminium and calcium may be under-estimates. The analyses of the solids are given in Table 58 (Page 167), although obvious outliers in individual results have been excluded from the summary.

In general, the results of our analysis and independent analysis compare well, although there are the usual differences in quantification for different elements which arise as a result of different analytical methods (sample preparation and analysis), as well as the use of different sample aliquots of an inherently inhomogeneous sample. The effect of sample inhomogeneity is seen if the results for APC residue and bottom ash are compared, with the relative standard deviations for the bottom ash generally being less good than the more uniform APC residue.

Although the relative standard deviations in any one sample set (year) are relatively high, these values (typically <15% for most elements) are quite reasonable figures for the analysis of different samples of the same residues, in some cases collected on different days, and the RSD's for our analysis are not significantly different from those obtained by the independent laboratory. The relative standard deviations are less good when data from three different studies are compared, suggesting systematic changes in the incinerator residue composition on different visits, and possibly changes to the analytical method affecting quantification. However, the overall value of the data is improved by the relatively high number of samples used, and provides a useful cross-check that the results obtained in this study are in broad agreement with previous work on waste incinerators.

Summary

The data obtained for most elements are generally in good agreement with the available literature on the composition of incinerator residues. These results indicate that the CEML is capable of making quantitative measurements of the metals of interest in normal "liquids analysis" mode, and provides evidence that the incinerator plant was operating normally during the monitoring periods. However, the results do not indicate temporal variations in the system operation, and so the need for continuous monitoring of incinerator gases is seen. Along with continuous monitoring data, these analyses of solid samples help to establish a full picture of the occurrence and distribution of metals in the municipal solid waste incinerator being studied, and to provide verification of the measurements made using our laboratory. The overall findings for distribution of different metals are given individually in Chapter 6.

Table 58: Comparison of average results for the analysis of a number of samples of incinerator residues for metal content in-house and by an independent laboratory

Sample	Year	Value	Number samples	of Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Sb	Si	Sn	V	Zn
APC Residue independent laboratory	**2002**	**Average (PPM)**	**5**	**41900**	**21**		**720**	**250800**	**123**		**197**	**679**	**6640**	**20850**		**10680**	**468**	**13150**	**115**	**1198**		**64680**	**948**		**6680**
APC Residue independent laboratory	**2002**	**Relative Standard Deviation (%)**	**5**	**25**	**46**		**80**	**7**	**70**		**44**	**15**	**25**	**4**		**16**	**51**	**9**	**126**	**19**		**24**	**55**		**39**
APC Residue	2002	Average (PPM)	7	34894		81	598	220780	103	57	78	914	6896	27191	31	9755	483	22466	110	2705			951	250	7326
APC Residue	2002	Relative Standard Deviation (%)	7	15		13	17	10	14	18	9	4	22	11	8	8	13	7	20	14			12	16	13
APC Residue	2004	Average (PPM)	6	35291	15	72	307	180213	69		70	563	7485	18484	39	8042	593	9616	48	1736	197		462	137	6827
APC Residue	2004	Relative Standard Deviation (%)	6	7	6	5	13	6	2		5	7	7	5	3	5	4	4	5	3	10		4	4	3
APC Residue	2005	Average (PPM)	1	22426			505	194355	78	47	85	424	5981	16930	15	6763	512	9303	25	1387	107		419	112	4139
APC Residue	**2005**	**Relative Standard Deviation of 3 repeats of 1 sample (ppm)**		**1**			**2**	**1**	**2**	**2**	**1**	**3**	**2**	**4**	**7**	**2**	**2**	**1**	**5**	**3**	**5**		**2**	**3**	**1**
APC Residue	**All**	**Average (PPM)**	**14**	**34174**	**15**	**77**	**466**	**201507**	**86**	**56**	**75**	**728**	**7097**	**22727**	**33**	**8735**	**532**	**16019**	**77**	**2196**	**184**		**703**	**192**	**6884**
APC Residue	**All**	**Relative Standard Deviation (%)**	**14**	**15**	**6**	**12**	**35**	**13**	**23**	**18**	**9**	**27**	**16**	**22**	**20**	**14**	**13**	**42**	**49**	**27**	**21**		**38**	**35**	**15**
Fly ash prior to lime injection	2004	Average (PPM)	2	37660				129411	38	36	116	351	38194	13663	37	8381	760	8490	67	886			1057	98	6663
Fly ash prior to lime injection	2004	Relative Standard Deviation (%)	2					31	33	30	11	14	31	6	20	5	0	5	13	2			7		4
Fly ash prior to lime injection	2005	Average (PPM)	5	33378		98	603	140559	32	31	122	368	5475	17375	19	8826	693	7768	40	771	56		324	96	3404
Fly ash prior to lime injection	2005	Relative Standard Deviation (%)	5	9		9	10	10	5	12	16	16	9	11	9	10	22	12	14	12	17		18	8	16
Fly ash prior to lime injection	2005	Relative Standard Deviation of 3 repeats of 1 sample (ppm)		2		2	0	3	3	3	3	1	2	1	1	3	3	0	3	2	8		5	2	3
Fly ash prior to lime injection	**All**	**Average (PPM)**	**7**	**34091**		**98**	**603**	**136843**	**34**	**33**	**120**	**363**	**16381**	**16138**	**24**	**8678**	**712**	**7974**	**48**	**804**	**56**		**568**	**96**	**4335**
Fly ash prior to lime injection	**All**	**Relative Standard Deviation (%)**	**7**	**10**		**9**	**10**	**16**	**19**	**18**	**14**	**14**	**108**	**15**	**39**	**8**	**18**	**11**	**30**	**12**	**17**		**67**	**8**	**38**
Bottom Ash independent laboratory	**2002**	**Average (PPM)**	**3**	**58200**	**22**		**900**	**120000**	**46**		**211**	**3688**	**64400**	**12467**		**11333**	**839**	**9267**	**118**	**926**		**165333**	**3238**		**4200**
Bottom Ash independent laboratory	**2002**	**Relative Standard Deviation (%)**	**3**	**12**	**16**		**29**	**8**	**23**		**3**	**4**	**28**	**7**		**10**	**8**	**12**	**41**	**14**		**9**	**145**		**19**
Bottom Ash	2002	Average (PPM)	6	42743		39	334	72604	32	4	75	1943	54868	4273	15	7091	608	6747	81	1371			1094	191	873
Bottom Ash	2002	Relative Standard Deviation (%)	6	31		45	43	12	40	15	31	66	44	12	24	12	64	21	36	19			142	20	36
Bottom Ash	2004	Average (PPM)	4	42350		67	472	60740	25	40	67	2098	44270	3221	27	5698	785	2490	71	1104			593		2531
Bottom Ash	2004	Relative Standard Deviation (%)	4	65				43		41	36	13	44	7	19	20	35	5	5	23			76		50
Bottom Ash	2005	Average (PPM)	1	125778		91	654	74538		32	55	2934	46998	5645	17		618	3997	71	1117			864	93	2430
Bottom Ash	2005	Relative Standard Deviation of 3 repeats of 1 sample (ppm)		2		2	0	3		6	1	3	1	5	3		1	3	6	2			2	3	3
Bottom Ash	**All**	**Average (PPM)**	**11**	**42568**		**49**	**391**	**68864**	**31**	**21**	**70**	**2160**	**51638**	**4075**	**20**	**6599**	**673**	**5195**	**77**	**1240**			**921**	**186**	**1973**
Bottom Ash	**All**	**Relative Standard Deviation (%)**	**11**	**53**		**58**	**52**	**38**	**50**	**97**	**42**	**54**	**50**	**37**	**45**	**35**	**54**	**52**	**41**	**42**			**128**	**44**	**60**

Notes: Ag, Be, Tl and Hg were below Limit of Detection throughout the analyses

5.3 Continuous Measurement of Atmospheric Emissions from a MSW Incinerator

5.3.1 Summary of Data Obtained

Metal concentrations in the emitted cleaned flue gas of a municipal waste incinerator were measured on two occasions. The first study concentrated on metal levels in cleaned gas, and the system was optimised and calibrated for very low concentration measurements. The second study centred on measurements in un-cleaned gas, and limited confirmatory measurements were made in the emitted gas.

Although the results obtained on the two occasions were similar, it is evident that measurements of very low metal concentrations can be optimised when the system is configured for "clean" gas monitoring, rather than using system parameters designed for un-cleaned gas monitoring. This meant that the baseline corrections were much better when the system was optimised for clean gas monitoring, and the low-concentration calibration was also better, which should generally lead to better quantification. However, due to instrument control constraints, it was only possible to monitor a limited number of emission lines during the earlier monitoring of cleaned flue gas, which was completed using an earlier software version. In some cases, the line selected for "clean-gas" monitoring was not the most sensitive, and thus the choice of emission line was revised prior to further work. Therefore it means that for some metals, detection limits obtained for cleaned flue gas were not as low as could be obtained later.

Despite the generally improved measurement parameters in clean gas when the instrument was optimised for this task, measurements of cleaned gas during the un-cleaned monitoring had definite value: Firstly, it helped to indicate that the system was essentially giving similar emissions during the two experimental campaigns, which were about 18 months apart. Secondly, it helped to determine realistic instrumental detection limits for measurements in un-cleaned gas (see section 5.4.1). Thirdly, it helped to show the direct improvement in pollutant concentration in the flue gas before and after clean-up, as the measurements were directly comparable.

Measured concentrations of all metals in the cleaned flue gases, on either experimental campaign, were found to be extremely low. Some variation was seen in some of the concentration profiles, but for many, the measured signal was essentially at or below the limit of detection throughout, and thus only baseline (zero) fluctuation was observed. Assessment of the accuracy of quantification was made by periodically introducing calibration check standards to the instrument during on-line monitoring, using the ultra-sonic nebuliser in the laboratory. These checks are seen in the emission profiles, and are referred to in Table 59.

During the week of monitoring dedicated to emitted gas emissions, nearly 60 hours of data were obtained. The instrument could be operated un-attended, and emissions profiles for periods of over 24 hours could be obtained un-interrupted. For the longer monitoring period, some baseline drift was observed for metals very near zero concentration, although sensitivity was otherwise good. Given that this affects many different elements (not all), it seems likely to be caused by changing USN characteristics, or changing plasma parameters. In the cleaned flue gas measurement campaign, fluctuations were not closely linked to bulk plant conditions. Measured concentrations of different metals are shown in Table 59, along with an indication of temporal variation. Individual concentration profiles for different metals are shown in section 5.3.2 - 5.3.21.

Table 59: Estimated detection limits, typical element concentrations and experimental error in measurements in emitted flue gas

Element	Monitor line (nm)	Detection limit in flue gas [3 σ] (mg m^{-3})	Maximum variation from average caused by changing carbon dioxide concentration [0-20] (%)	Average metal concentration in un-cleaned gas for a 12 hour period (mg m^{-3})	Signal variation [relative standard deviation] for a 12 hour period ()	Calibration check error (%)	Estimated error in measured values (%) (empirical estimate from known errors)	Line suitability?
Aluminium	396.152	0.0011	±10	0.0234	1.4	± 50	±50	Sensitivity excellent but quantitative accuracy in variable matrix an issue.
Antimony	206.833	0.159	± 20	0.0120	214	±10 for large spikes, smaller not detected	± 100	Sensitivity poor, matrix interference very problematic, LOD not obtained during run
Arsenic	189.042	0.361	±100	0.2485	37	±30	±100	No – sensitivity poor, matrix interference very high
Cadmium	226.503	0.150	±20	0.0033	408	± 20 for large spike, more for smaller	±100 or more	Interference from matrix and poor line sensitivity mean quantification is poor. However, calibration checks show a peak would easily be detected, were it emitted
Calcium	393.366	0.0013	±20	0.0070	108	±20	±25	Yes. However, there may be interference from Ca contamination in water supply, leading to fluctuation seen in latter half of profile
Chromium	283.563	0.0027	-	0.0062	8.2	±10	±10	Yes if true LOD reached
Cobalt	238.892	0.0027	-	0.0208	4.5	±5	±10	Yes if true LOD reached
Copper	324.754	0.0001	±10	0.0006	12.2	±25	±30	Sensitivity excellent but quantification (calibration) could be better
Iron	259.941	0.002	±20	0.0022	45.6	±10	±20	Yes if true LOD reached, some interference from matrix change evident (c.f. Calcium profile)
Lead	261.418	0.123	±5	0.0272	43.1		NA- detection limit not reached	Yes if LOD was ever reached, but 405nm line would have been better (sensitivity and matrix problems)
Magnesium	285.213	0.0002	±5	0.0010	46.8	±30 typical	±30	Sensitivity excellent, quantification sensitive to matrix changes
Manganese	257.611	0.0056	±20	0.0242	2.01	±30	±30	Yes, though systematic error may be introduced through calibration imperfections
Mercury	253.653	0.112	±10	0.0088	61.8	±40	±50	Interference from matrix and low line sensitivity mean LOD is high. However, calibration checks show a peak would easily be detected, were it emitted, even if quantification were imperfect
Nickel	341.476	0.0011	±10	0.0097	1.7	± 30 typical	±30	Sensitivity excellent, quantification sensitive to matrix changes
Potassium	766.491	0.0012	±20	0.0036	39.0	± 30 typical	±30	Sensitivity excellent where LOD reached, but quantification sensitive to matrix changes
Sodium	589.592	0.080	± 20	0.0731	312.	±30	±30	Yes, but measurements near or around LOD
Thallium	276.787	1.56	±10	0.04	8763	±100+	-	Sensitivity very low, matrix interference high. Most of time, theoretical LOD not reached, and quantification extremely suspect even when it is
Tin	242.949	0.043	±5	0.0087	144	±30 for large peaks, more for smaller	-	Poor sensitivity, LOD not normally reached. 303nm would have been better, but peaks would have been seen, were they present
Vanadium	309.311	0.0013	±20	0.0011	23.2	±10 for large peaks, more for smaller	±	Yes if true LOD reached, matrix variability raises LOD over quoted figure
Zinc	213.856	Line not sensitive to Zn, even during calibration. Line itself ok, so peak selection may have been at fault						

5.3.2 Aluminium

Figure 68 shows the measured emissions of aluminium in a 24 hour period. Emissions are found to be extremely small, though the emission line is highly sensitive, and the detection limit low. Essentially, there is no significant aluminium detected in the cleaned gas. The sections indicated with red arrows on this, and subsequent figures, are where calibration checks were completed, along with other instrumentation checks. Therefore, the measurements recorded are not of actual metal emissions, and these peaks should be ignored when assessing the atmospheric metal emissions.

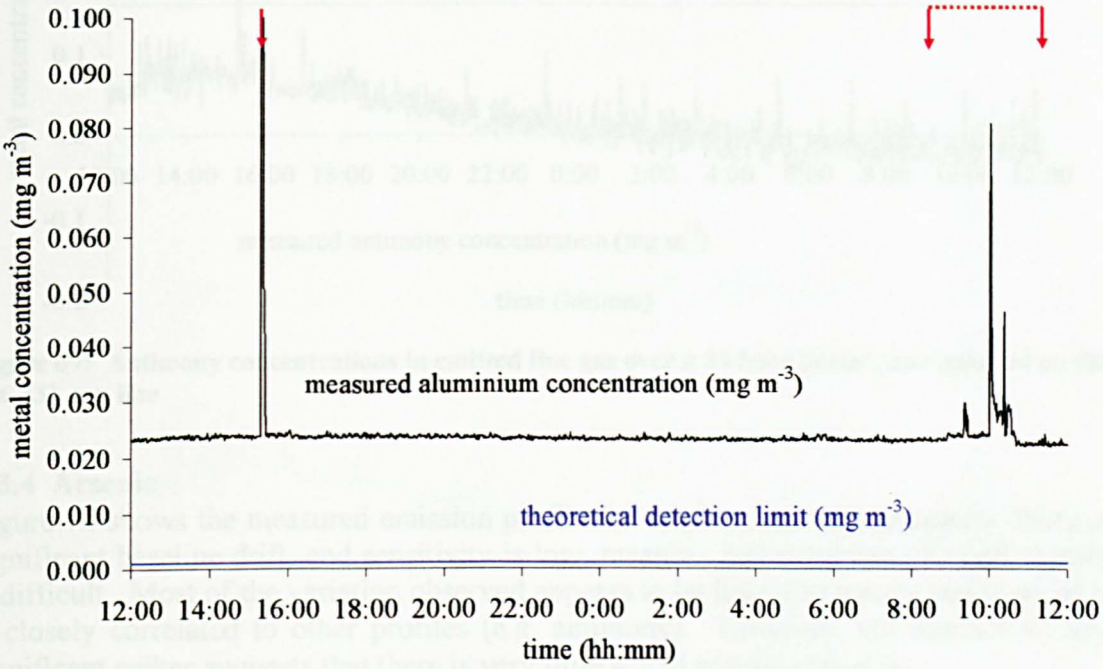


Figure 68: Aluminium concentrations in emitted flue gas over a 24 hour period, as measured on the 213.856 nm line

5.3.3 Antimony

Figure 69 shows the measured emission profile for antimony. Although some temporal fluctuations are seen, there is significant baseline drift, and the detection limit is high. This, along with the failure to observe the second calibration check standards, suggests that the line is not sufficiently sensitive for measurements in cleaned flue gas, and there appears to be significant matrix interference at low concentrations.

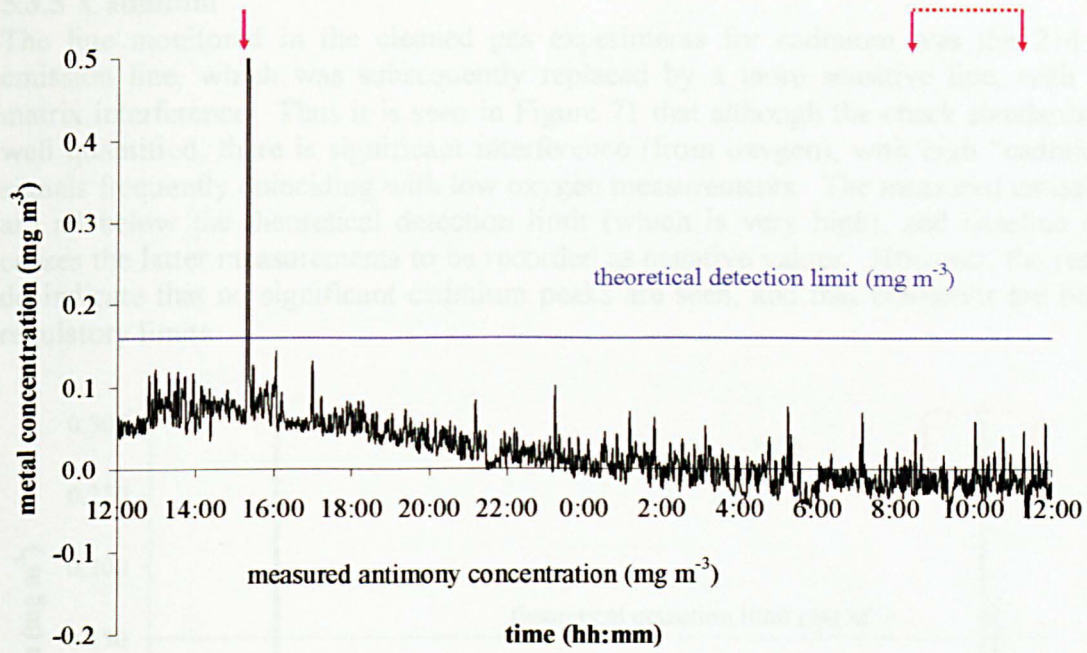


Figure 69: Antimony concentrations in emitted flue gas over a 24 hour period, as measured on the 206.833 nm line

5.3.4 Arsenic

Figure 70 shows the measured emission profile for arsenic. As with antimony, there is significant baseline drift, and sensitivity is low, meaning that detection of small signals is difficult. Most of the variation observed appears to be linked to matrix variation, as it is closely correlated to other profiles (e.g. antimony). However, the absence of any significant spikes suggests that there is very little actual arsenic emission.

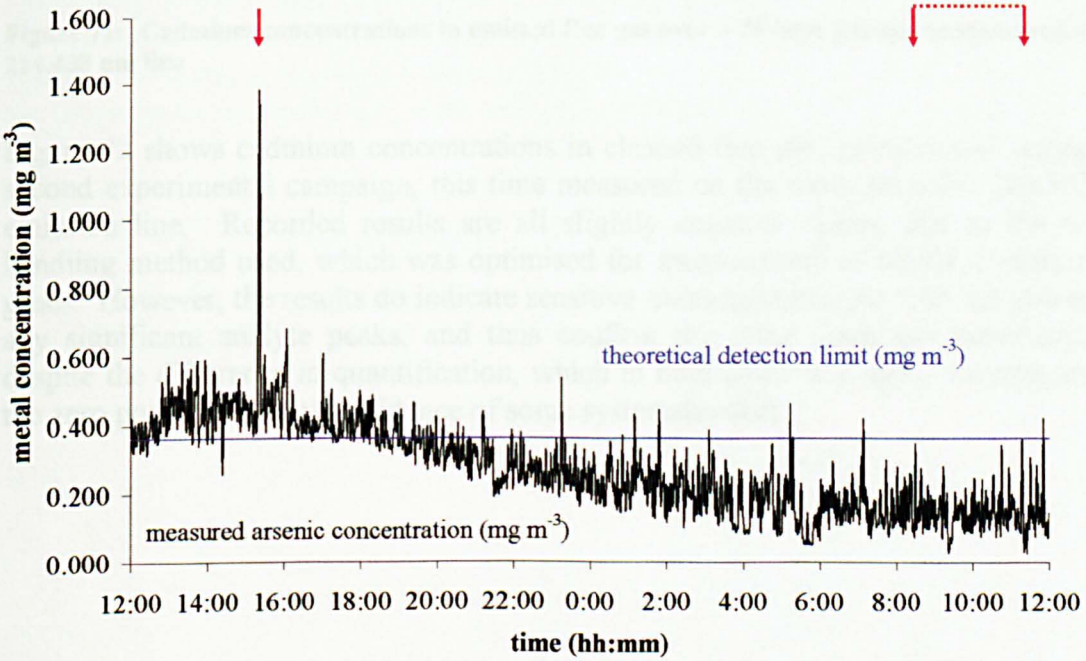


Figure 70: Arsenic concentrations in emitted flue gas over a 24 hour period, as measured on the 189.042 nm line

5.3.5 Cadmium

The line monitored in the cleaned gas experiments for cadmium was the 214 nm emission line, which was subsequently replaced by a more sensitive line, with less matrix interference. Thus it is seen in Figure 71 that although the check standards are well quantified, there is significant interference (from oxygen), with high "cadmium" signals frequently coinciding with low oxygen measurements. The measured emissions are all below the theoretical detection limit (which is very high), and baseline drift causes the latter measurements to be recorded as negative values. However, the results do indicate that no significant cadmium peaks are seen, and that emissions are below regulatory limits.

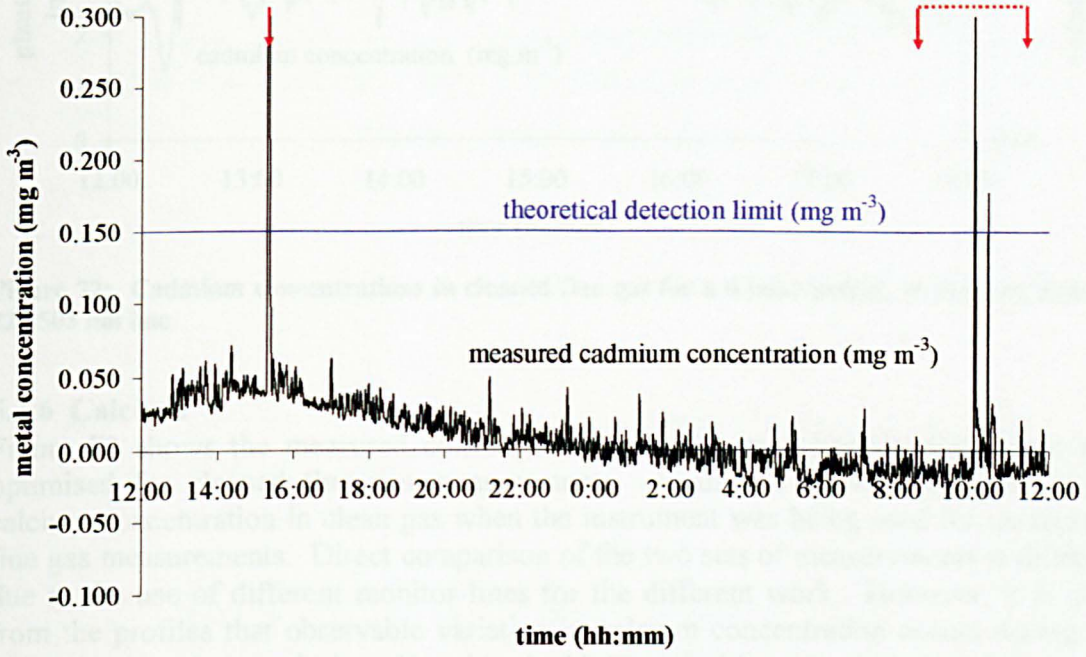


Figure 71: Cadmium concentrations in emitted flue gas over a 24 hour period, as measured on the 214.438 nm line

Figure 72 shows cadmium concentrations in cleaned flue gas, as measured during the second experimental campaign, this time measured on the more sensitive 226.503 nm emission line. Recorded results are all slightly negative values, due to the results handling method used, which was optimised for measurement of highly contaminated gases. However, the results do indicate sensitive measurements, but with the absence of any significant analyte peaks, and thus confirm the other clean gas measurements, despite the difference in quantification, which in both cases is a signal varying around the zero position, with the evidence of some systematic drift.

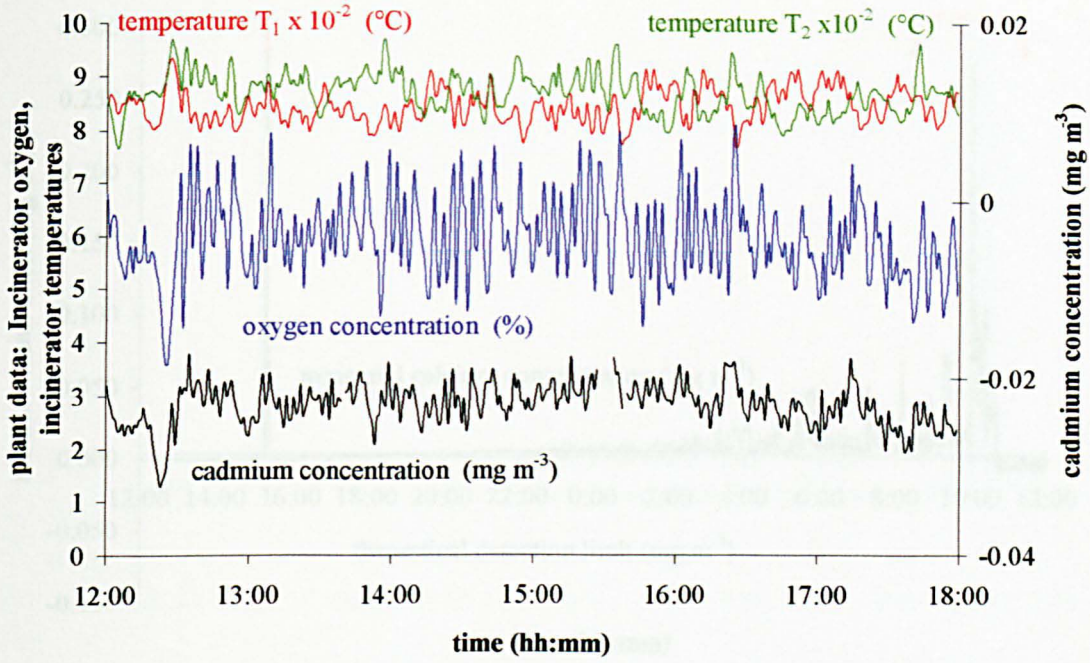


Figure 72: Cadmium concentrations in cleaned flue gas for a 6 hour period, as measured on the 226.503 nm line

5.3.6 Calcium

Figure 73 shows the measured concentrations of calcium, when the instrument was optimised for cleaned flue gas measurements. Figure 74 shows measurements of calcium concentration in clean gas when the instrument was being used for un-cleaned flue gas measurements. Direct comparison of the two sets of measurements is difficult, due to the use of different monitor lines for the different work. However, it is clear from the profiles that observable variation in calcium concentration occurs during the monitoring period, and that detection is highly sensitive, as demonstrated by the calibration peaks. While the quantification at near zero concentration is poor when the system is optimised for high contamination levels, measurements optimised for clean gas show good quantification, with low drift, and generally being above the detection limit.

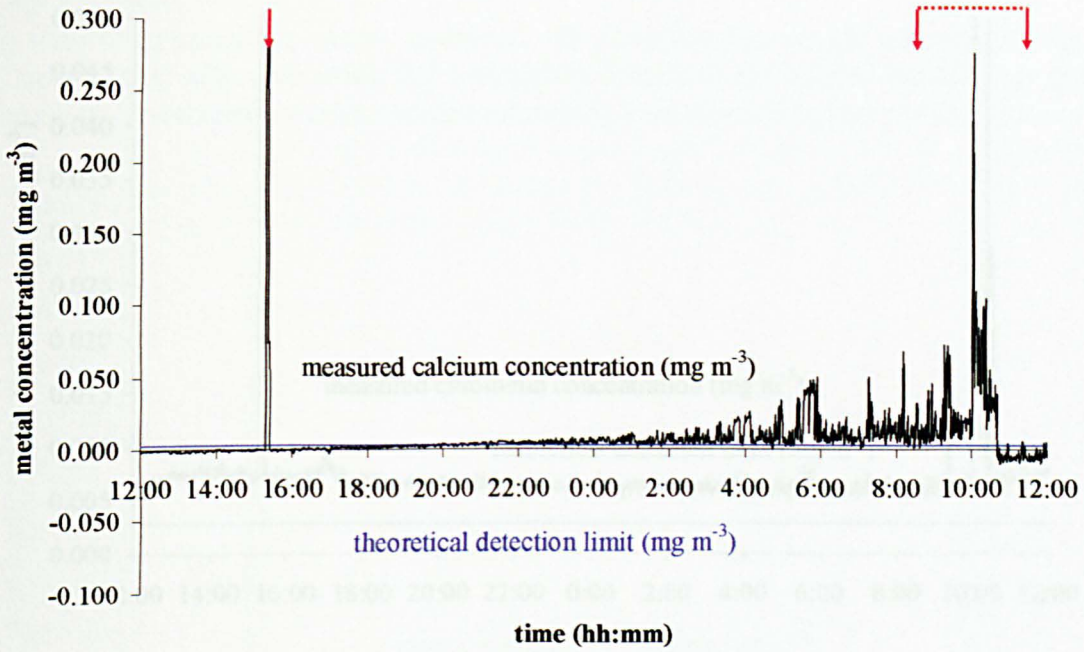


Figure 73: Calcium concentrations in emitted flue gas over a 24 hour period, as measured on the 393.366 nm line

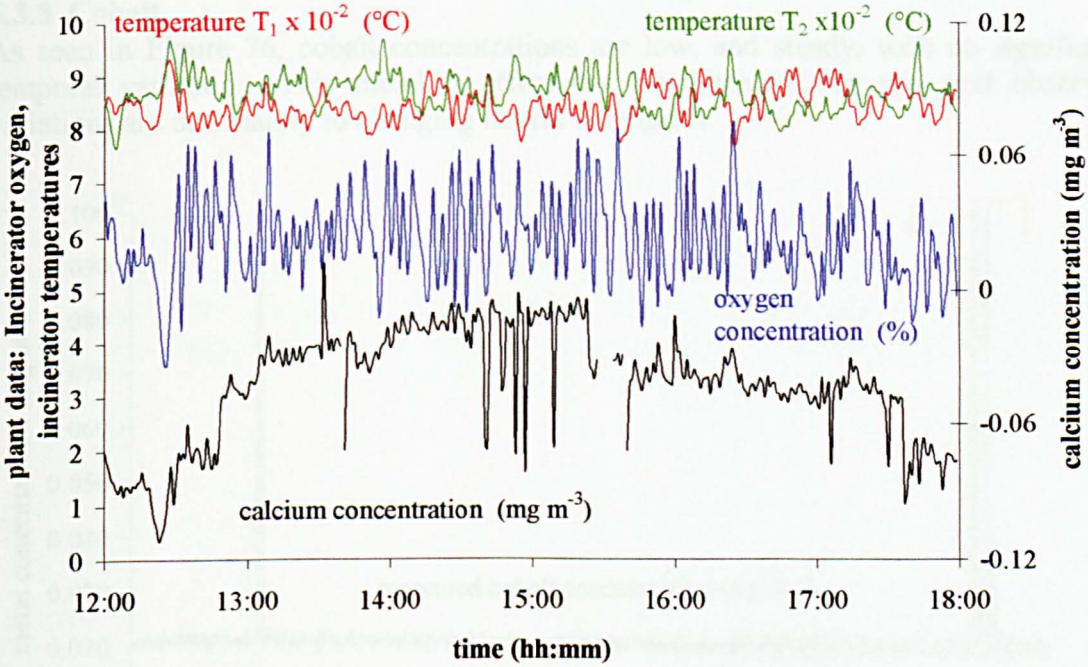


Figure 74: Calcium concentrations in cleaned flue gas for a 6 hour period, as measured on the 422.673 nm line

5.3.7 Chromium

Figure 75 shows chromium concentrations measured in clean flue gas while the instrument was optimised for such measurements, The profile shows near-zero concentrations of the element, with the calibration checks showing high sensitivity, with detection limits being easily exceeded.

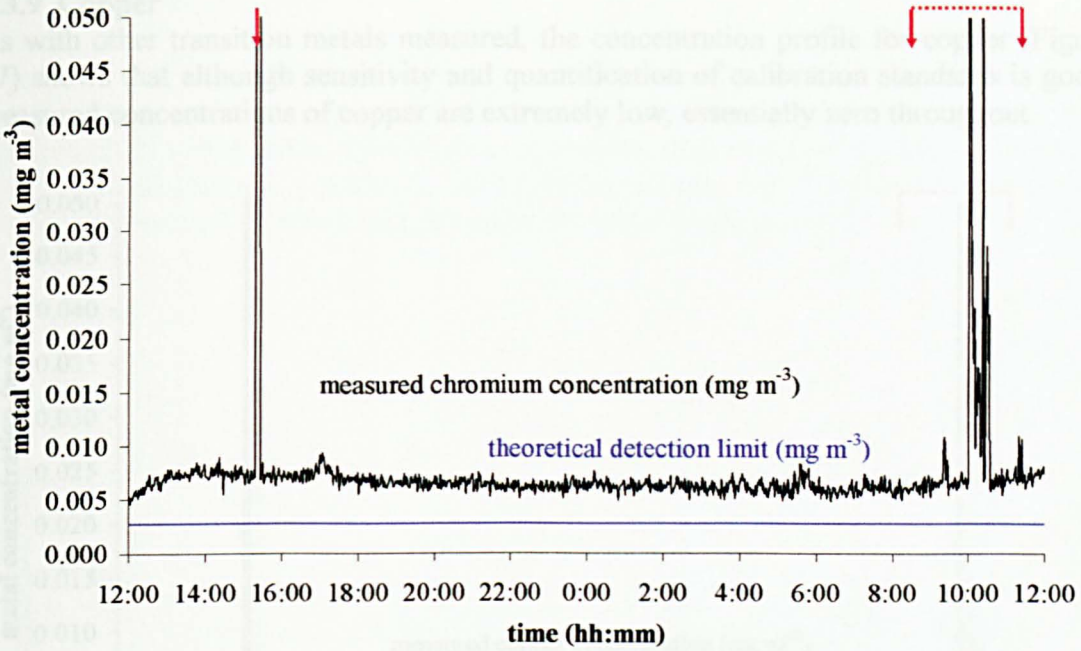


Figure 75: Chromium concentrations in emitted flue gas over a 24 hour period, as measured on the 283.563 nm line

5.3.8 Cobalt

As seen in Figure 76, cobalt concentrations are low, and steady, with no significant temporal variation. This metal is effectively not seen in flue gas, and observed variations are due mainly to changing matrix conditions.

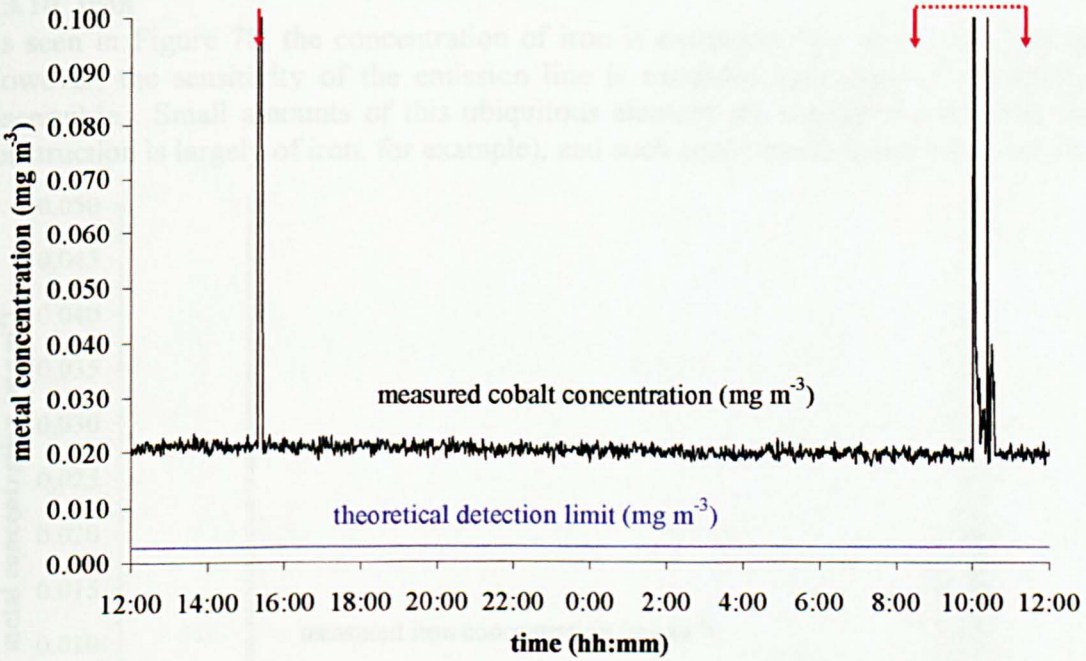


Figure 76: Cobalt concentrations in emitted flue gas over a 24 hour period, as measured on the 238.892 nm line

5.3.9 Copper

As with other transition metals measured, the concentration profile for copper (Figure 77) shows that although sensitivity and quantification of calibration standards is good, measured concentrations of copper are extremely low, essentially zero throughout.

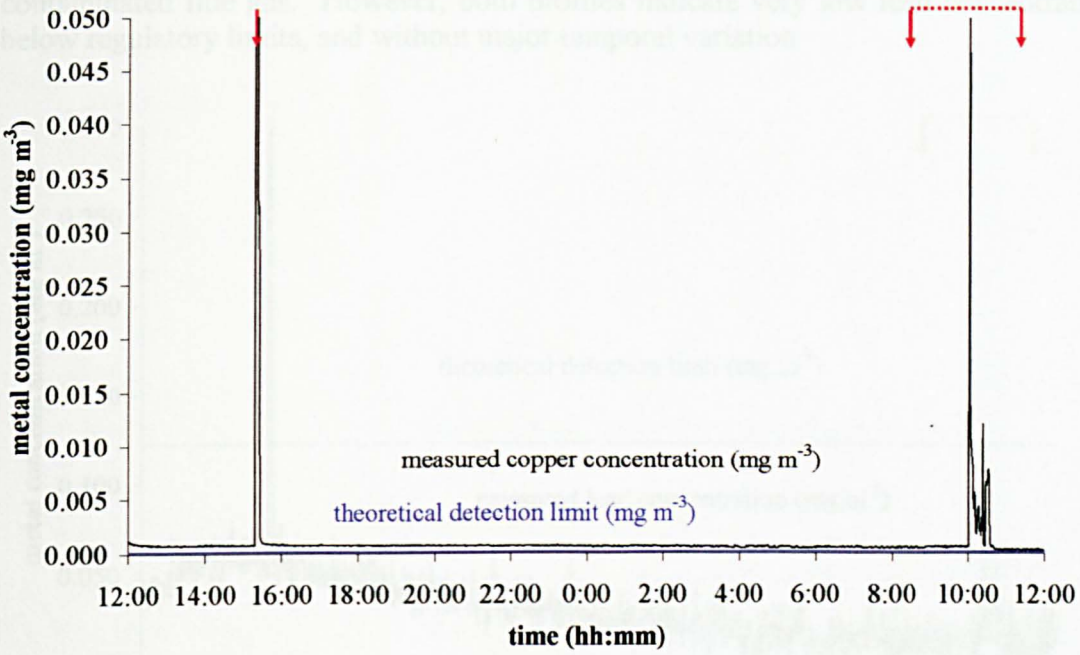


Figure 77: Copper concentrations in emitted flue gas over a 24 hour period, as measured on the 324.754 nm line

5.3.10 Iron

As seen in Figure 78, the concentration of iron is extremely low in cleaned flue gas. However, the sensitivity of the emission line is excellent, and temporal variation is discernible. Small amounts of this ubiquitous element are not unexpected (the plant construction is largely of iron, for example), and such concentrations are not of concern.

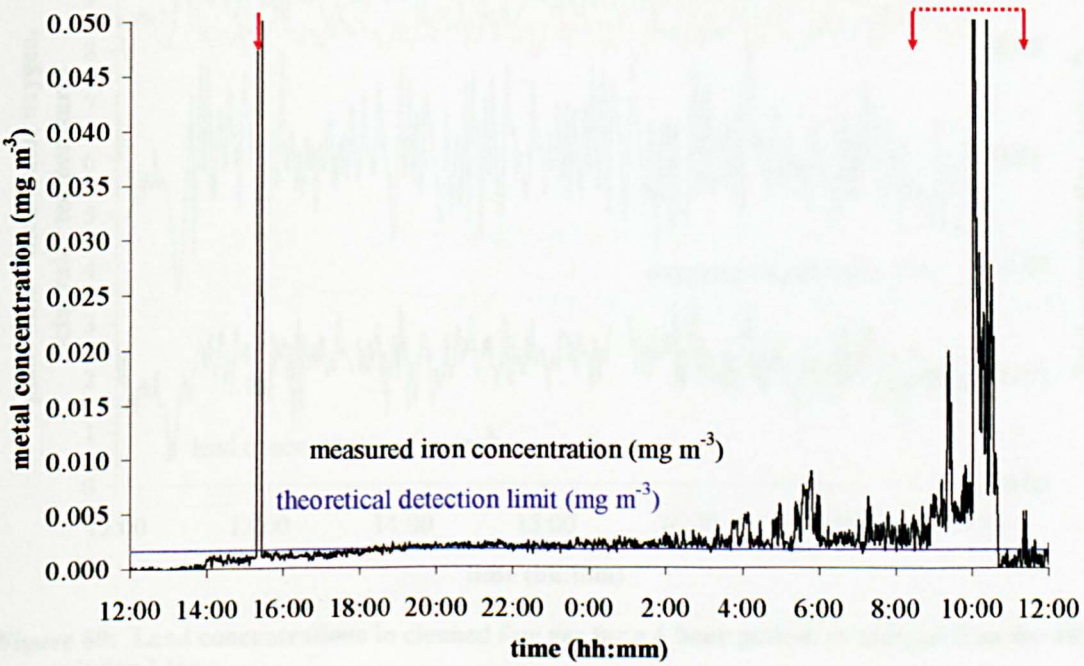


Figure 78: Iron concentrations in emitted flue gas over a 24 hour period, as measured on the 259.940 nm line

5.3.11 Lead

Figure 79 and Figure 80 show the measured lead emissions. Sensitivity of the line used in the first set of measurements was low, and quantification of the second calibration peak is poor. Once more, there is some systematic drift in measurements optimised for contaminated flue gas. However, both profiles indicate very low lead concentrations, below regulatory limits, and without major temporal variation.

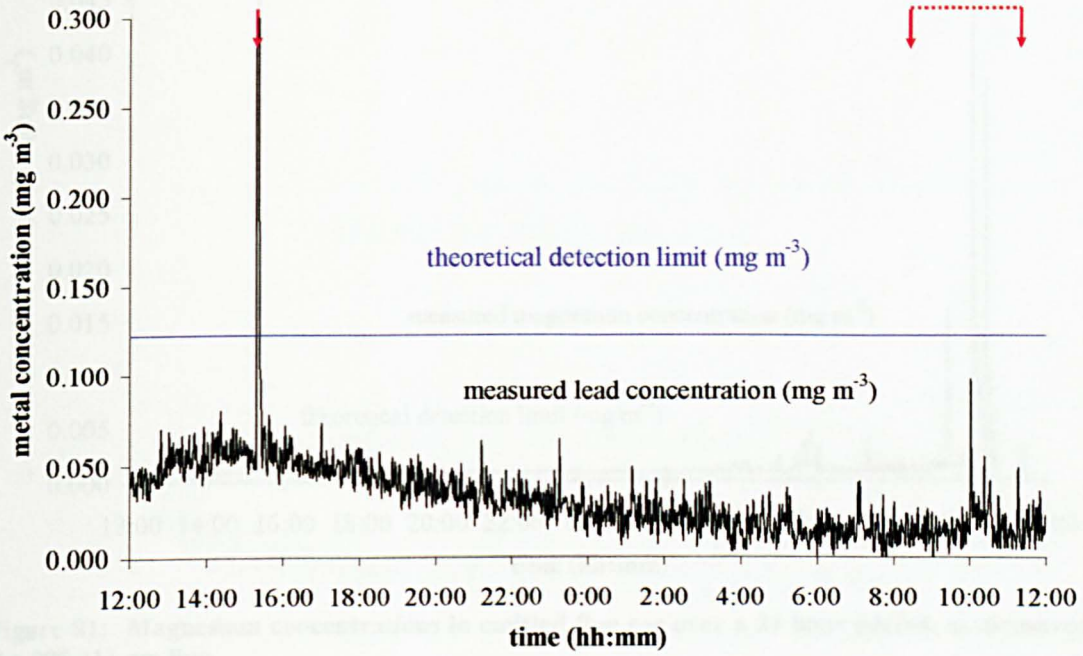


Figure 79: Lead concentrations in emitted flue gas over a 24 hour period, as measured on the 261.418 nm emission line

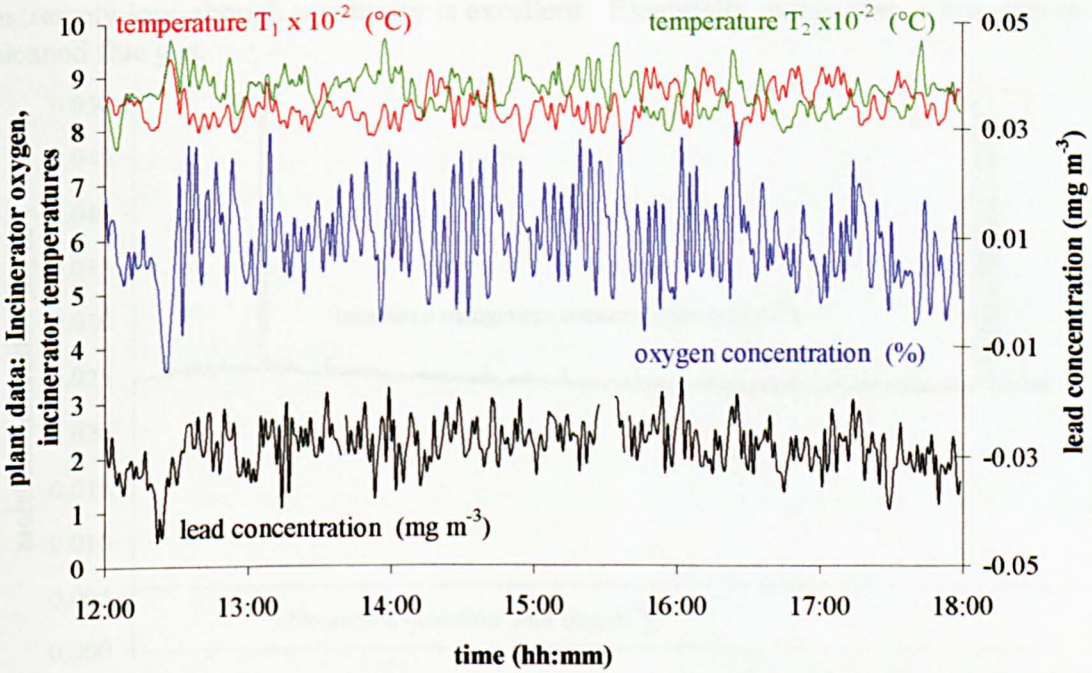


Figure 80: Lead concentrations in cleaned flue gas for a 6 hour period, as measured on the 405.778 nm emission Line

5.3.12 Magnesium

Figure 81 indicates magnesium concentrations measured in cleaned flue gas. Measurements show good sensitivity, and indicate low magnesium concentrations apart from the calibration checks. Nevertheless, some variation is seen in magnesium concentration.

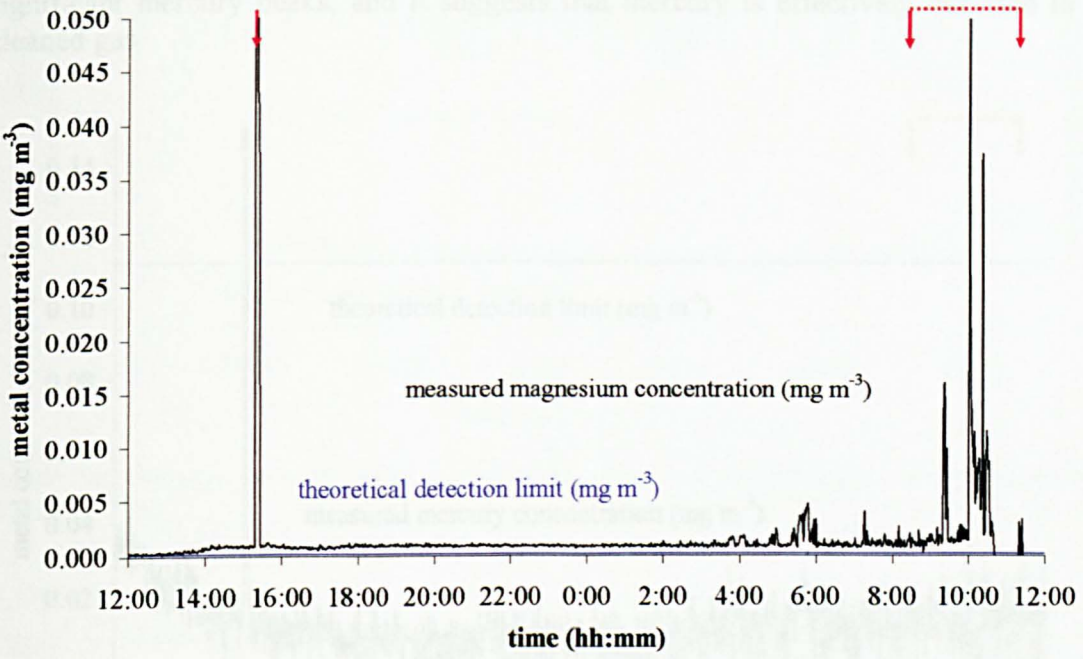


Figure 81: Magnesium concentrations in emitted flue gas over a 24 hour period, as measured on the 285.213 nm line

5.3.13 Manganese

Measured concentrations of manganese are shown in Figure 82. Concentrations are extremely low, though sensitivity is excellent. Essentially manganese is not seen in the cleaned flue gas.

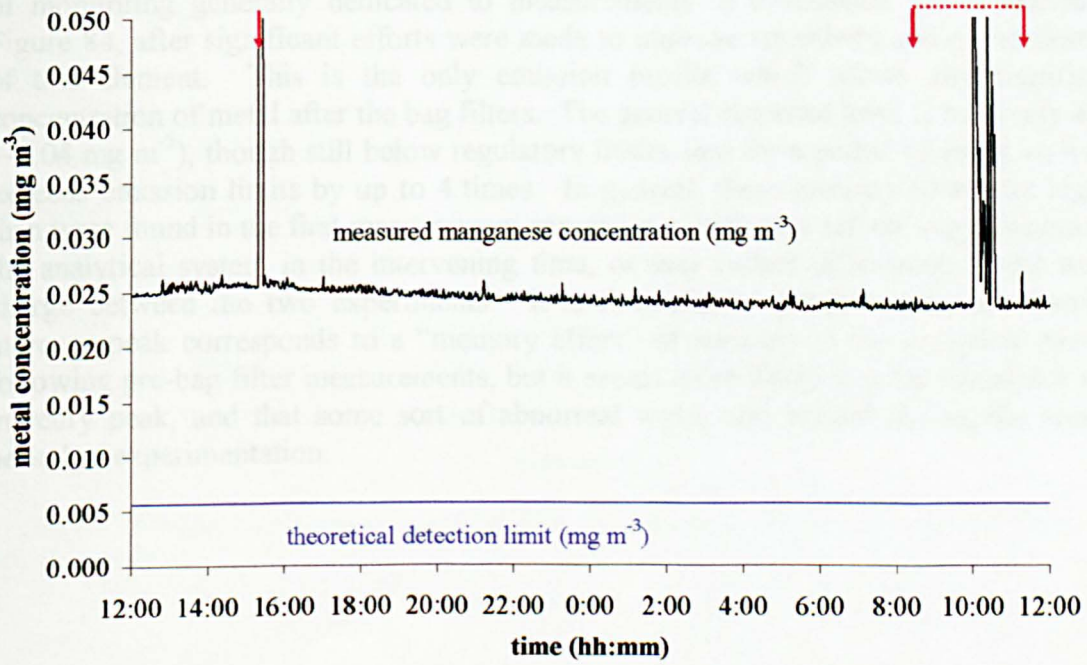


Figure 82: Manganese concentrations in emitted flue gas over a 24 hour period, as measured on the 257.610 nm line

5.3.14 Mercury

Measured mercury concentration beyond the bag filters in the monitoring period dedicated to clean-gas monitoring are low, though some baseline drift is observed, as seen in Figure 83. Although concentrations are below the effective limit of detection, due to the low sensitivity of the available emission lines, it is clear that there are no significant mercury peaks, and it suggests that mercury is effectively not seen in the cleaned gas.

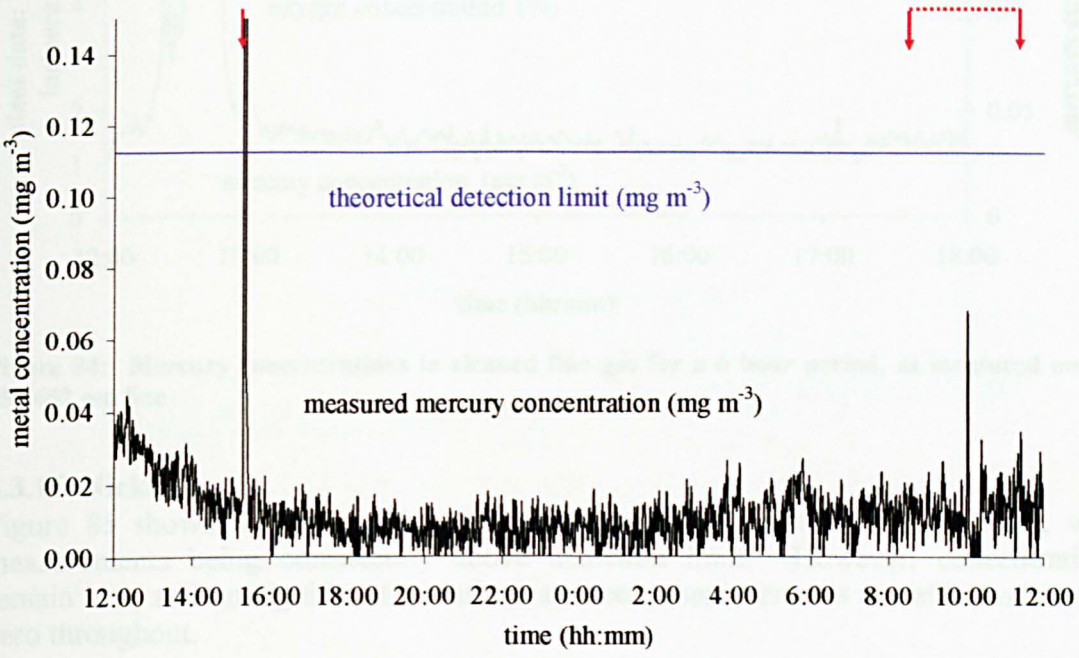


Figure 83: Mercury concentrations in emitted flue gas over a 24 hour period, as measured on the 253.652 nm line

In contrast, the emission profile for mercury measured in clean flue gas during the week of monitoring generally dedicated to measurements in un-cleaned gas is shown in Figure 84, after significant efforts were made to improve sensitivity and quantification of this element. This is the only emission profile which shows any significant concentration of metal after the bag filters. The general recorded level is relatively high (~0.04 mg m^{-3}), though still below regulatory limits, and for a period of about an hour, exceeds emission limits by up to 4 times. In general, these mercury levels are higher than were found in the first measurement campaign, which may reflect improvements in the analytical system in the intervening time, or may reflect differences in the waste charge between the two experiments. It is theoretically possible that the observed mercury peak corresponds to a "memory effect" of mercury in the analytical system following pre-bag filter measurements, but it seems more likely that the signal is a true mercury peak, and that some sort of abnormal waste was burned during the second period of experimentation.

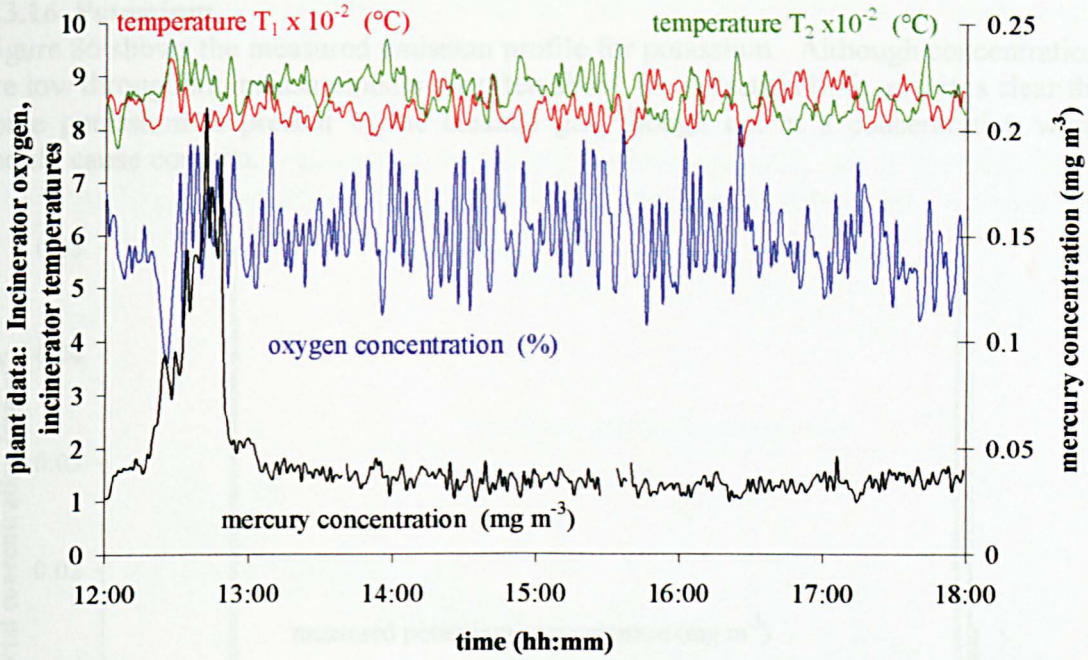


Figure 84: Mercury concentrations in cleaned flue gas for a 6 hour period, as measured on the 253.652 nm line

5.3.15 Nickel

Figure 85 shows the measured emissions for nickel. Sensitivity is excellent, with measurements being consistently above detection limit. However, concentrations remain low, and no significant variations are seen; measurements are effectively near-zero throughout.

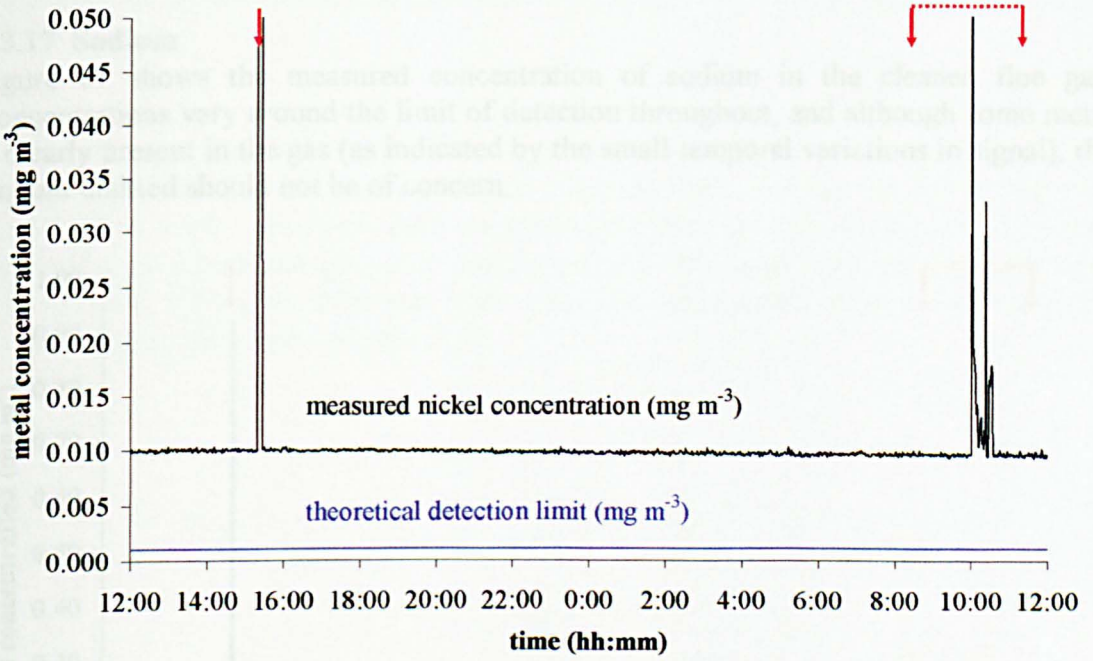


Figure 85: Nickel concentrations in emitted flue gas over a 24 hour period, as measured on the 341.476 nm line

5.3.16 Potassium

Figure 86 shows the measured emission profile for potassium. Although concentrations are low throughout, measurements are often above the detection limit, and it is clear that some potassium is present in the cleaned gas, though not at a concentration which should cause concern.

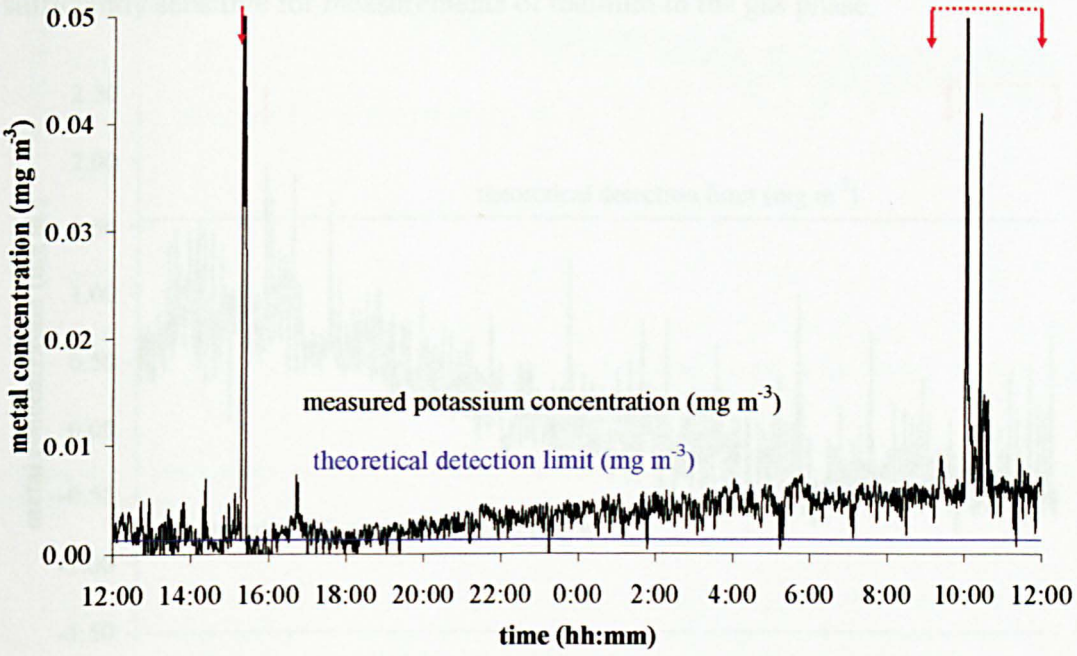


Figure 86: Potassium concentrations in emitted flue gas over a 24 hour period, as measured on the 766.490 nm line

5.3.17 Sodium

Figure 87 shows the measured concentration of sodium in the cleaned flue gas. Concentrations vary around the limit of detection throughout, and although some metal is clearly present in the gas (as indicated by the small temporal variations in signal), the amount emitted should not be of concern.

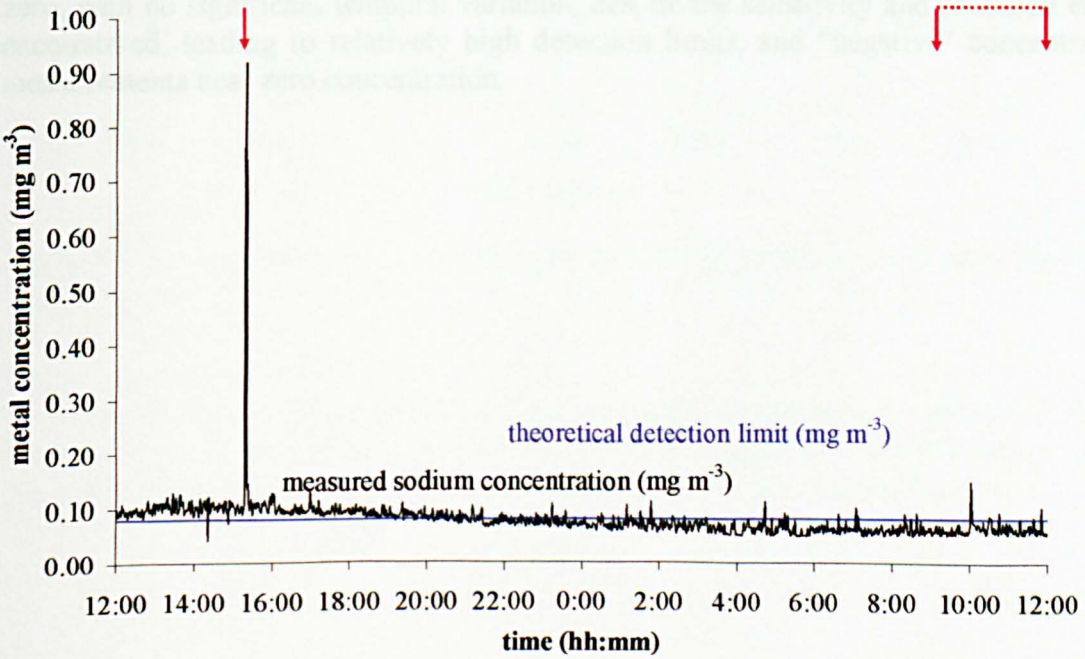


Figure 87: Sodium concentrations in emitted flue gas over a 24 hour period, as measured on the 589.592 nm line

5.3.18 Thallium

Although an attempt was made to measure a thallium emission line (Figure 88), neither of the calibration check peaks was seen clearly, and it was evident that the line was not sufficiently sensitive for measurements of thallium in the gas phase.

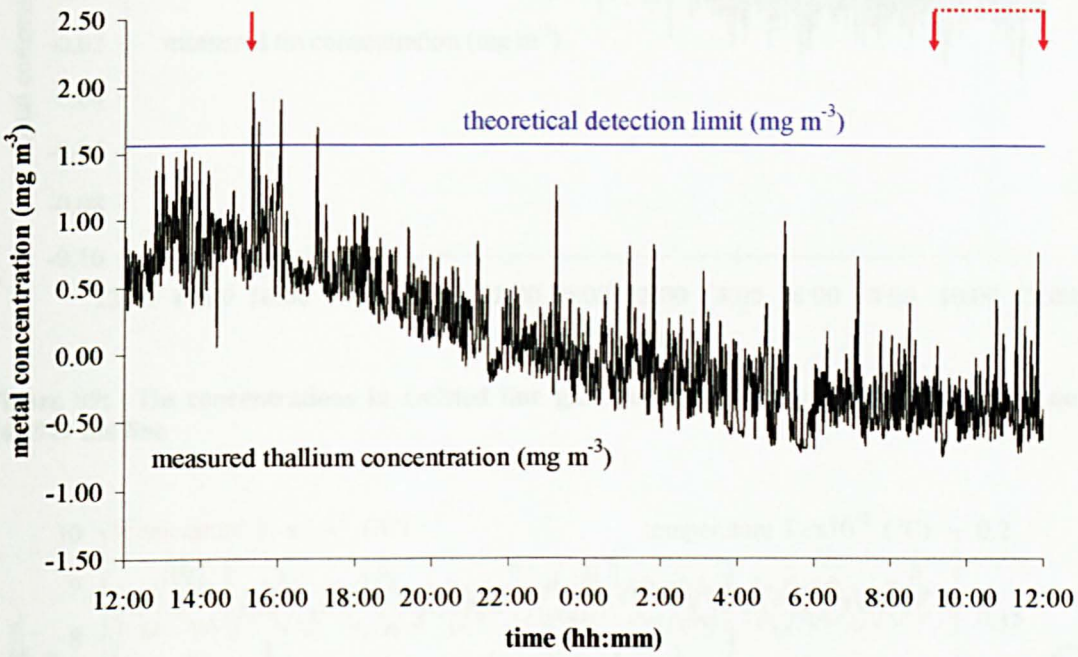


Figure 88: Thallium concentrations in emitted flue gas over a 24 hour period, as measured on the 190.864 nm line

5.3.19 Tin

Figure 89 and Figure 90 show measurements of tin in un-cleaned flue gas. The sensitivity of the 242 nm line was found to be relatively low, so the 303 nm line was used in later work. However, both measurements show tin concentrations to be around zero, with no significant temporal variation, despite the sensitivity and precision errors encountered, leading to relatively high detection limits, and "negative" concentration measurements near zero concentration.

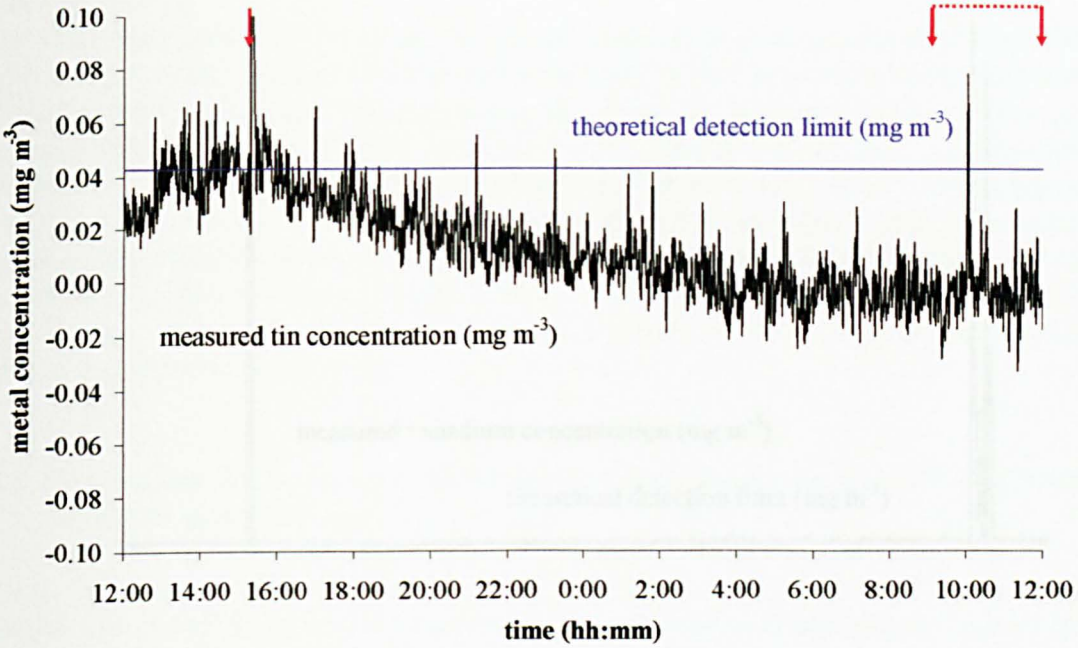


Figure 89: Tin concentrations in emitted flue gas over a 24 hour period, as measured on the 242.949 nm line

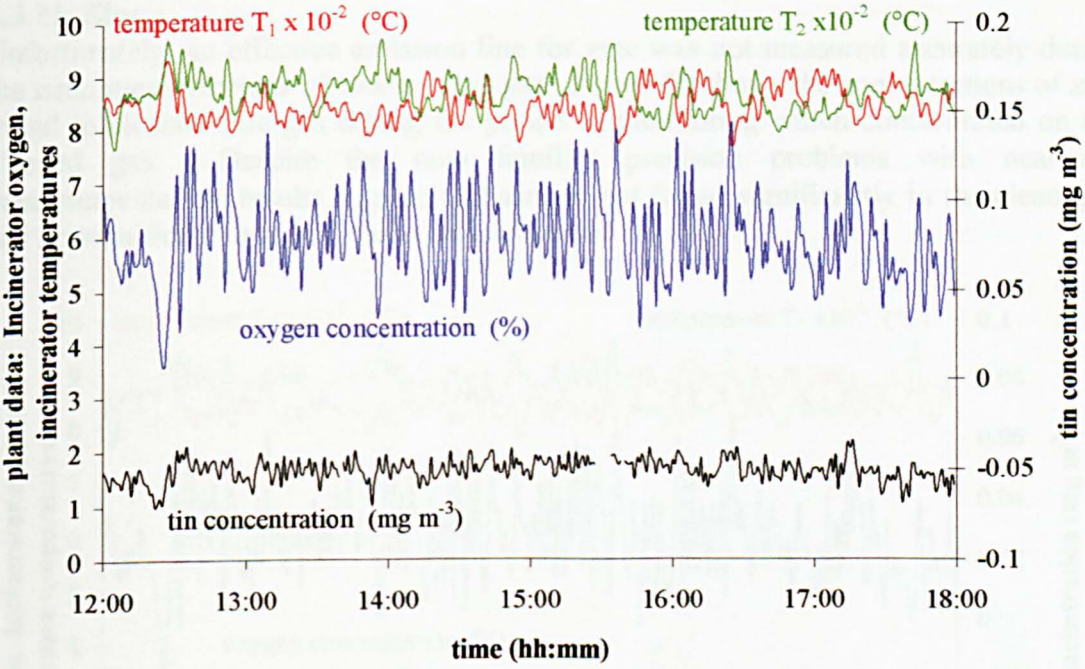


Figure 90: Tin concentrations in cleaned flue gas for a 6 hour period, as measured on the 303.412 nm line

5.3.20 Vanadium

As shown in Figure 91, the measured concentrations of vanadium are extremely small, varying near-zero, and around the limit of detection, despite the excellent sensitivity of the monitor line. Effectively, vanadium was not found in the cleaned flue gas.

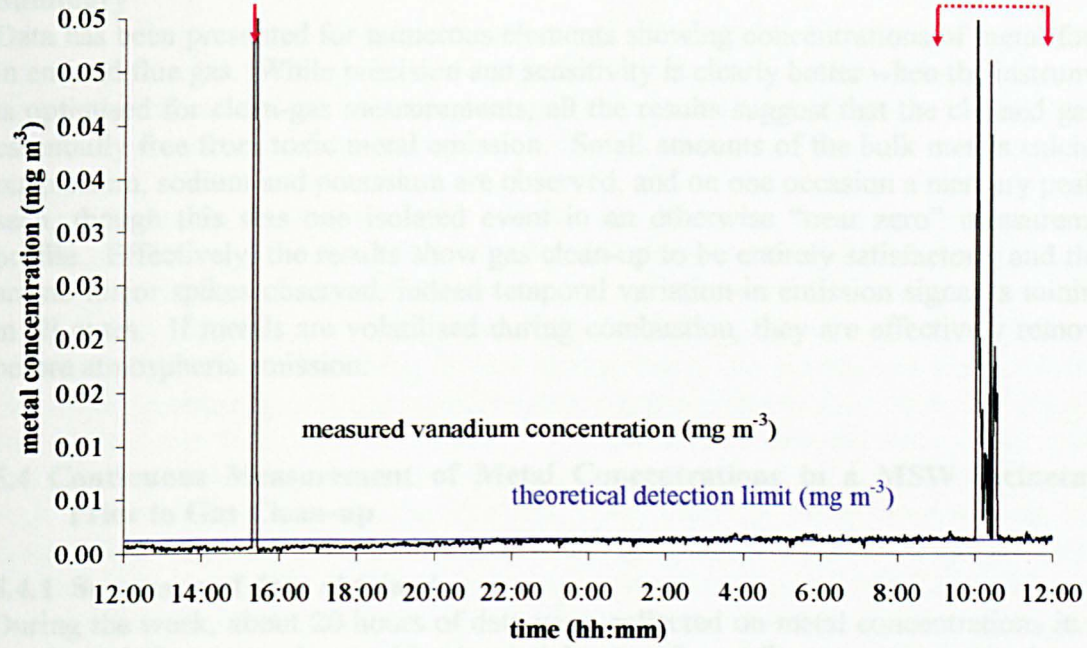


Figure 91: Vanadium concentrations in emitted flue gas over a 24 hour period, as measured on the 309.311 nm line

5.3.21 Zinc

Unfortunately, an effective emission line for zinc was not measured accurately during the main measurements of cleaned flue gas. Figure 92 shows the concentrations of zinc found in cleaned flue gas during the period of monitoring which concentrated on un-cleaned gas. Despite the now familiar precision problems with near-zero measurements, the results suggest that zinc is not found significantly in the clean gas, and no significant temporal variation is observed.

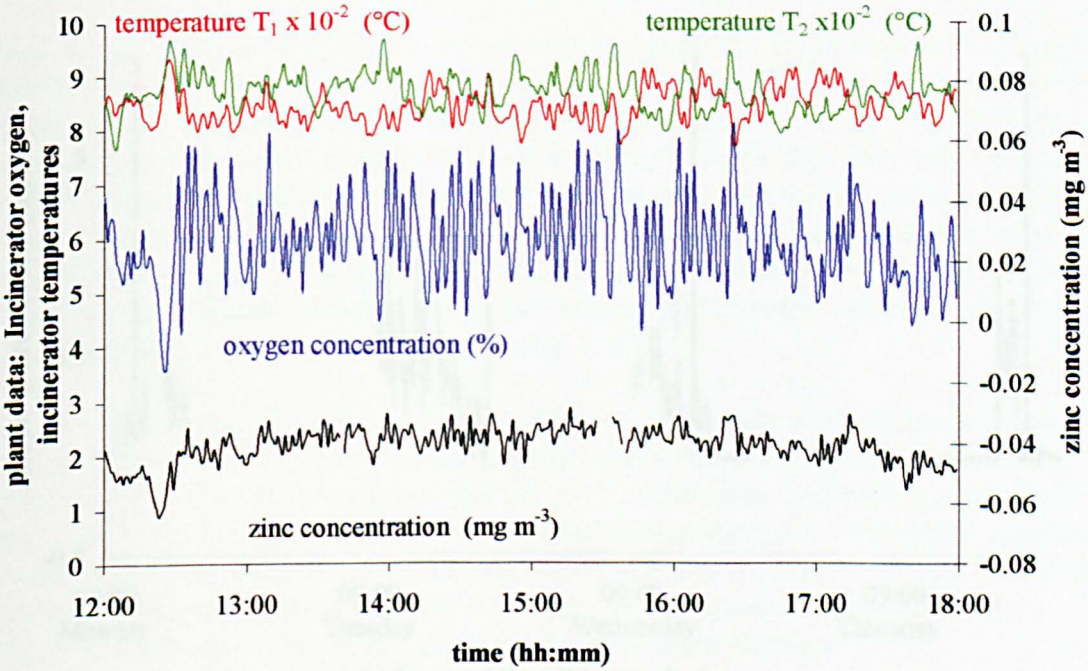


Figure 92: Zinc concentrations in cleaned flue gas for a 6 hour period, as measured on the 213 nm line

Summary

Data has been presented for numerous elements showing concentrations of metal found in emitted flue gas. While precision and sensitivity is clearly better when the instrument is optimised for clean-gas measurements, all the results suggest that the cleaned gas is essentially free from toxic metal emission. Small amounts of the bulk metals calcium, magnesium, sodium and potassium are observed, and on one occasion a mercury peak is seen, though this was one isolated event in an otherwise "near zero" measurement profile. Effectively, the results show gas clean-up to be entirely satisfactory, and there are no major spikes observed, indeed temporal variation in emission signal is minimal in all cases. If metals are volatilised during combustion, they are effectively removed before atmospheric emission.

5.4 Continuous Measurement of Metal Concentrations in a MSW Incinerator Prior to Gas Clean-up

5.4.1 Summary of data obtained

During the week, about 20 hours of data were collected on metal concentrations in the un-cleaned flue gas, along with about 6 hours of post-flue gas treatment data for comparison. Figure 93 shows typical results obtained for the whole week of on-site monitoring, in this case for lead measured on the 405.778 nm emission line. Measurements in highly polluted, particulate laden gas show high concentrations of volatile metals, and there is significant temporal variation in concentration. However, because of the challenging analytical conditions, measurements could not be made when the instrument was unattended, as frequent checks were required to ensure that the sample line cleanliness and integrity was maintained. Thus it was rare for monitoring to continue uninterrupted for more than two hours, more typically there being a "down-time" of a few minutes every half hour or so, and monitoring could not continue overnight. Thus the data obtained differs significantly in magnitude and volume from those in cleaned gas.

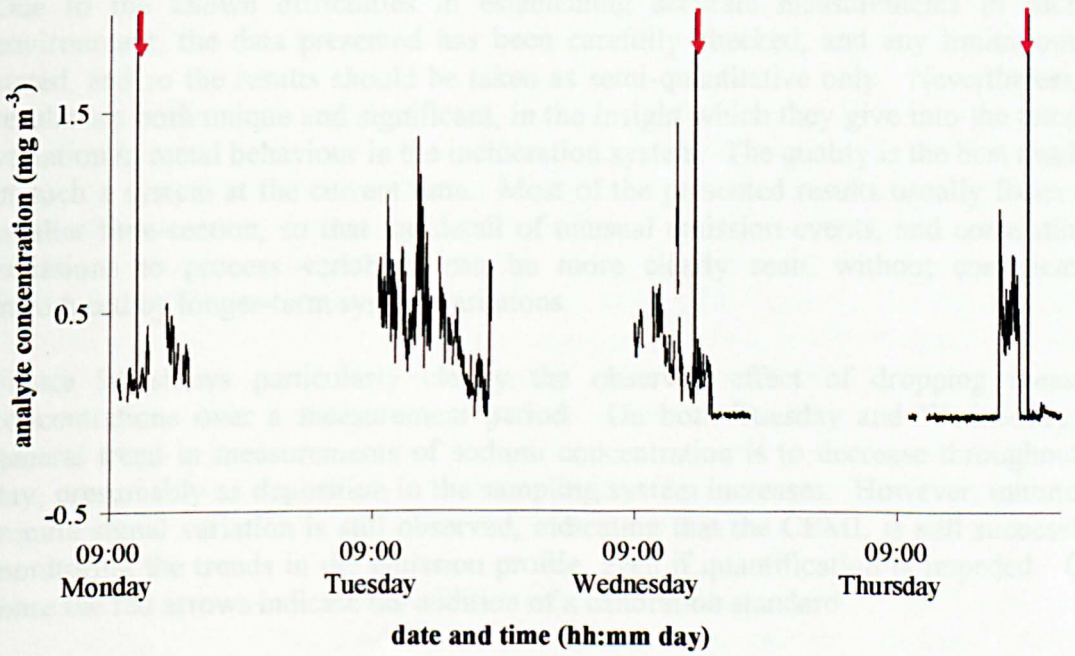


Figure 93: Results obtained for the whole week analytical measurements: Concentration of lead measured on the 405 nm emission line

At three points on Figure 93, the measured "emission" goes off the graph scale. These events correspond to the addition of an on-line standard check. Four general regions of high metal concentration are seen, corresponding to the four days on which on-line monitoring was successfully conducted on flue gas prior to clean-up.

Measurements taken on Wednesday evening and Thursday morning are seen to have much lower analyte concentrations. For this period, the sample line (following thorough cleaning), was transferred to a post bag-filter monitoring location, to measure cleaned, emitted flue gas. About 6 hours of successful data were collected, following several problems re-establishing on-line monitoring. The system had been optimised for pre-bag measurements, and so unfortunately some of the element lines, including the one shown for lead, record "negative concentrations" due to sub-optimal results handling methods. This is because the system was optimised for good quantification of high metal concentrations in the flue gas, rather than for good baseline (near zero) resolution, with changes to the results handling systems (calibration range, way of dealing with matrix CO_2 variation -linear regression or manual correlations). Of course, the condition of the clean-up system may also have altered in the intervening time (age, cleanliness of the bag filters), which will also affect the results.

However, the overall trend is quite clear: the metal concentrations beyond the bag filters are extremely small and without major temporal variation, in stark contrast to measurements made prior to clean-up.

Care should be exercised in interpretation of the data for un-cleaned gas, due to the extremely challenging analytical conditions. For example, in an extended run of several hours, measured values can often be seen to gradually drop through the day, presumably due to particulate fouling of the sampling system, leading to deposition of some of the analytical sample, and so reduced measured values. Nevertheless, the variation observed in the data is far more that is attributable to this source alone.

Due to the known difficulties in establishing accurate measurements in such an environment, the data presented has been carefully checked, and any limitations are stated, and so the results should be taken as semi-quantitative only. Nevertheless, the results are both unique and significant, in the insight which they give into the temporal variation in metal behaviour in the incineration system. The quality is the best available in such a system at the current time. Most of the presented results usually focus on a smaller time-section, so that the detail of unusual emission events, and correlation of emissions to process variables, can be more clearly seen, without complications introduced by longer-term system variations.

Figure 94 shows particularly clearly the observed effect of dropping measured concentrations over a measurement period. On both Tuesday and Wednesday, the general trend in measurements of sodium concentration is to decrease throughout the day, presumably as deposition in the sampling system increases. However, minute-by-minute signal variation is still observed, indicating that the CEML is still successfully monitoring the trends in the emission profile, even if quantification is impeded. Once more the red arrows indicate the addition of a calibration standard.

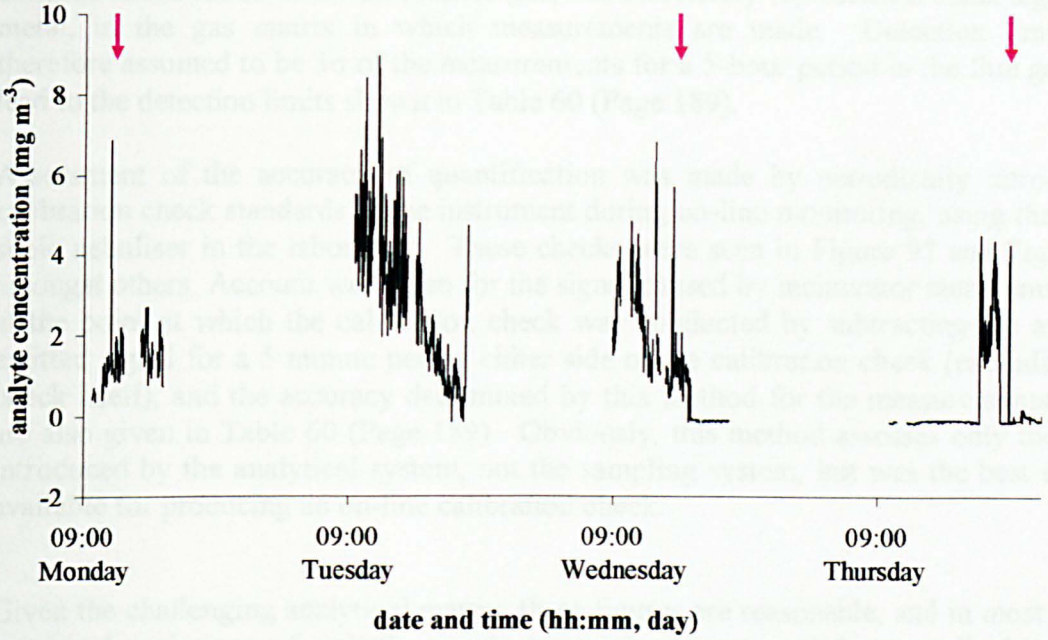


Figure 94: Results obtained for the whole week analytical measurements: Concentration of sodium on the Na 589.592 nm emission line

Numerous metals were detected in the raw flue gas at high concentrations (1-10 mg m^{-3}), some with significant temporal variability. Others were detected simultaneously at concentrations several orders of magnitude lower (0-0.01 mg m^{-3}). Some metal concentrations, and their fluctuations could be correlated to some extent with plant (combustion chamber) conditions. Other variations were believed to correspond to changes in the waste feed and local combustion conditions on the burning bed. However, a full mathematical correlation of final metal concentrations to known factors was not possible, nor was really expected, given the complex and heterogeneous nature of the combustion system. The average metal concentration found for numerous different metals, along with an indication of temporal variation, is given in Table 59. Emission profiles for different metals are given in 5.4.2.

Accuracy of Quantification and Detection Limits

Given the variations in measured signals, which are known to be introduced by the changing gas matrix in an industrial combustion system, it is extremely difficult to assess the accuracy of the measurements obtained, and to estimate the true detection limit of the instrument (i.e. the change in signal which is unambiguously due to changing metal concentration, rather than to instrument "noise"). In this situation, a theoretical detection limit from the calibration procedure is hardly a useful indicator of practical detection limit, because it clearly under-estimates the error associated with measurements in the real system (normally in analytical chemistry, the limit of detection is taken to be 2, 3, or 5 times the standard deviation (σ)of the blank signal, as determined during calibration, and quantification in the calibrated range of the instrument is assumed to be accurate to within a few percent).

The rather pragmatic solution proposed for this highly unusual gas matrix, where changing carbon dioxide concentration causes changes in detection limit and instrument sensitivity is therefore as follows. Limited on-line monitoring of cleaned flue gas, beyond the bag filters, was conducted for about 5 hours, and although some small amount of metal may have been present in the cleaned gas, compared with the high

concentrations found in the un-cleaned gas, this effectively represents a blank signal for metal, in the gas matrix in which measurements are made. Detection limits are therefore assumed to be 3σ of the measurements for a 5-hour period in the flue gas, and lead to the detection limits shown in Table 60 (Page 189).

Assessment of the accuracy of quantification was made by periodically introducing calibration check standards to the instrument during on-line monitoring, using the ultra-sonic nebuliser in the laboratory. These checks were seen in Figure 93 and Figure 94 amongst others. Account was taken for the signal caused by incinerator metal emissions at the point at which the calibration check was conducted by subtracting the average emitted signal for a 5 minute period either side of the calibration check (excluding the check itself), and the accuracy determined by this method for the measurements made are also given in Table 60 (Page 189). Obviously, this method assesses only the error introduced by the analytical system, not the sampling system, but was the best system available for producing an on-line calibration check.

Given the challenging analytical matrix, these figures are reasonable, and in most cases, measured emissions of volatile metals (certainly during peaks) are well above this detection limit, showing that the analytical system is fit for the intended purpose. Again, the estimated error in the measurements, while not being ideal, is adequate, in order to give a reasonable quantitative indication of metal concentration in the un-cleaned flue gas. For a developmental continuous emissions monitor, high accuracy is not normally, expected, with EPA guidelines indicating that a relative accuracy of $\pm$ 20% would be acceptable for cleaned gas (Lemieux et al., 1998).

Data Verification

Given the unique nature of the data obtained by continuous monitoring of highly contaminated flue gas, data verification was not straightforward. On-line calibration checks with aqueous standards introduced in the laboratory were good, but this did not assess the error associated with the sample line (although earlier experiments (section 3.3.3) with mercury injection in a furnace have addressed this to some degree, though not fully resolving issues relating to particulate transport). Ideally, all the results would be cross-checked against the reference method (US EPA method 29), but this was not possible. Nevertheless, the results obtained from this study are in good broad agreement with existing data in the literature, for the analysis of small particulates, and bulk bag-filter residue from waste incineration. These results may be compared by taking the ratio of one volatile metal to another, as shown in Table 61 (Page 190), with lead being used as a reference metal.

Table 60: Estimated detection limits, typical element concentrations and experimental error in measurements in un-cleaned flue gas

Element	Monitor line (nm)	Detection limit [3 σ] (mg m^{-3})	Average metal concentration in un-cleaned gas for a 4 hour period (mg m^{-3})	Signal variation [relative standard deviation] for a 4 hour period (%)	Calibration check [recovery of standard][1] (%)			Estimated error in measured values (%)	Line good for quantitative measurement?
				Check number	1	2	3		
Aluminium	396.152	0.0205	-0.039	-40.5	100.3	95.8	95.8	± 10	Yes if LOD reached
Antimony	206.833	0.0060	0.009	88.5	112.6	133.4	165.1	± 70[2]	No – quantification suspect
Arsenic	-	-	-	-	-	-	-	-	-
Cadmium	226.503	0.0062	0.014	190.1	82.0	97.7	98.5	± 20[3]	Yes
Calcium	422.673	0.0589	0.151	73.3	109.4	100.9	104.0	± 10	Yes
Chromium	283.563	0.0131	-0.046	-8.9	78.5	90.5	92.7	± 25	Possibly if LOD reached
Cobalt	237.862	0.0074	-0.028	-8.3	73.1	88.9	99.4	± 30[4]	Possibly if LOD reached
Copper	324.754	0.0057	0.089	34.2	75.3	78.7	79.0	± 25	Yes
Iron	259.941	0.0315	0.004	436.2	90.3	89.4	87.7	± 20	Yes when over LOD
Lead	405.778	0.0126	0.572	32.4	101.7	97.8	91.7	± 10	Yes
Magnesium	279.553	0.0275	-0.088	-13.8	104.5	94.9	100.1	± 10	Yes if LOD reached
Manganese	257.611	0.0119	-0.041	-8.6	79.3	90.5	106.4	± 20	Yes if LOD reached
Mercury	253.653	0.0143	0.028	17.1	-	76.9	95.5	± 25[3,4]	Possibly if LOD reached[5]
Nickel	221.648	0.0081	-0.009	-142.2	78.2	91.6	97.0	± 25	Possibly if LOD reached
Potassium	766.491	0.0766	8.15	32.3	-	112.1	100.1	± 20[4]	Yes
Sodium	589.592	0.0438	4.17	28.4	-	104.7	94.4	± 10[4]	Yes
Thallium	276.787	0.0130	-0.013	-33.8	85.3	94.7	103.0	± 20	Yes if LOD reached
Tin	303.412	0.0175	0.120	37.1	86.5	95.2	93.4	± 20	Yes
Vanadium	309.311	0.0116	-0.044	-8.12	75.4	85.3	86.6	± 25	Possibly if LOD reached
Zinc	213.856	0.0141	1.20	33.1	85.0	97.2	101.3	± 20	Yes

[1] Accounting for metal concentration in flue gas at that time

[2] Evidently antimony was not accurately quantitatively detected

[3] Quantification of these elements could have been improved by taking the average of a number of monitored lines, but raw line results are shown here

[4] Poor quantification of the first standard led to overall estimated average falling outside of the desired ±25, but if this standard is excluded, quantification is acceptable. The standard was less well quantified for elements suffering from high "memory effect", as the period of introduction was not long enough to get good stability.

[5] Line suffered poor quantification at high concentration due to saturation, at which point less sensitive 435.835 nm line became better.

Table 61: Comparison of concentrations of metals found by continuous monitoring of un-cleaned flue gas with analysis of comparable solids (in-house and literature values), standardised with respect to lead

element	CEML un-cleaned flue gas data [1]	incinerator ash particulates <2μm [2]	MSW boiler ash before lime injection [3]	our APC residue analysis [4]	comment
Al	0	0.165	2.50	15.6	presence of Al clearly size dependent and none of data is directly comparable
As	0	0.002	0.002	0.007	good agreement - As found only in trace amount in any incinerator waste stream
Ba	0	0.009	0.126	0.212	fair agreement - Ba not found in vapour/small particles, but found in significant amount in larger solids
Ca	0.248	0.237	11.0	91.8	CEM and small particulate data in excellent agreement. Ca figure in APC residue affected by lime injection
Cd	0.0227	0.011	0.024	0.039	good agreement - trace levels of Cd found in all residues (following evaporative transport)
Co	0	0.0001	0.001	0.025	good agreement - Co found only in trace amount, probably over-quantified in our solid analysis
Cr	0	0.005	0.056	0.034	fair agreement - Cr not found in vapour/small particles, but found in significant amount in larger solids
Cu	0.153	0.021	0.069	0.332	poor agreement - Cu transfer in the experimental plant seems higher than in plants examined in the literature, our solids and gas data consistent
Fe	0.007	0.093	1.87	3.23	fair agreement - little Fe found in vapour/small particles, but found more in larger solid residues
Hg	0.049	-	0.0005	-	not enough data to make comparison
K	14.4	-	1.90	10.4	poor agreement - K transfer in the experimental plant seems higher than in plants examined in the literature, our solids and gas data consistent
Mg	0	0.070	0.531	3.98	fair agreement - Mg not found in vapour/small particles, but found in significant amount in larger solids. Our solids analysis may be an over-estimate
Mn	0	0.015	0.041	0.24	fair agreement - Mn not found in vapour/small particles, but found in significant amount in larger solids, though our solids analysis may be an over-estimate
Na	7.19	1.01	2.09	7.30	poor agreement - Na transfer in the experimental plant seems higher than in plants examined in the literature, our solids and gas data consistent
Pb	1.00	1.00	1.00	1.00	all 1 by virtue of the comparison
Sb	0.0690	0.025	0.092	0.084	good agreement - trace levels of Sb found in all residues (following evaporative transport)
Sn	0.209	0.110	0.112	0.320	good agreement - significant levels of Sn found in all residues (following evaporative transport)
Zn	2.06	1.24	2.23	3.14	good agreement - significant levels of Zn found in all residues (following evaporative transport)

[1] (Table 59)
[2] (Greenberg et al., 1978)
[3] (Belevi and Moench, 2000b)
[4] (Table 58)

The results are generally in good agreement with one another, given the expected variation from study to study, and the known differences between the materials being compared. Four distinct behaviours are observed. For non-volatile bulk metals, mainly transported by entrainment (e.g. Ca, Fe, Mg), the analysis of vapour and small particulates in un-cleaned flue gas is not directly comparable with the bulk residues, but CEM data for gas and solid analysis compares favourably with data from other sources, giving similar values. For significantly volatile metals, (e.g. Cd, Sn, Zn) the data for gas, small particulates, and solid residues compares well, with all giving similar values. For trace non-volatile metals, (e.g. Ba, Cr, Mn) the data for small particulates and un-cleaned flue gas compares well (with both showing near-zero concentrations of these metals), and our solids data also compares well with literature values. Finally, for the bulk volatile metals (Na and K, and also Cu), the data comparison is less good. Our data indicate that the relative amount of these metals, both in the un-cleaned flue gas and solid residues is unusually high. However, as this trend is common both to our gas monitoring data and solids analysis (which was confirmed by analysis by an independent laboratory – see section 5.2), it is believed that this difference is caused by the specific nature of the plant being studied, which led to greater bulk metal volatilisation, rather than to a significant error in our analytical data. Thus overall it is seen that our data compares with information already available on the incineration process

Emission Profiles for Different Metals

For some volatile metals, a great deal of temporal variation was observed in the concentration-time profiles obtained from monitoring the un-cleaned flue gas, and it was evident that numerous factors were contributing to the overall metal volatilisation process.

However, in discussing the causes of the observed temporal variations in different metals, it was necessary to establish "reference points", of what constituted "normal" metal emission, which included variation due to changing bulk incinerator conditions. In the absence of specific data on the waste input, or local furnace conditions (which it is not normally possible to obtain), it was found that the emission of sodium and potassium could provide just such a reference point. Figure 95 shows the changing concentration profiles for sodium and potassium. Although the magnitudes of the concentrations differ by a factor of about 2, it is seen that for the majority of the time, the two lines overlay remarkably well, indicating that concentrations of the two metals are inter-dependent. Given that both metals are found reasonably evenly distributed in a variety of different wastes, and that their volatilisation is dependent on formation of the metal chloride (discussed elsewhere), it became apparent that the sodium emission profile could provide an indicator of the relative "bulk volatilisation conditions" on the burning bed, and that therefore an assessment of the degree of temporal variation in the emission of other metals could be made by comparison with the sodium profile. This is indicated in Figure 96, which shows that while the normalised potassium signal varies between 0.75 and 1.5 of a sodium concentration, normalised to 1 for each measurement, the lead emission varies between 0.5 and 2, indicating a much higher temporal variation which was not due to bulk incinerator conditions.

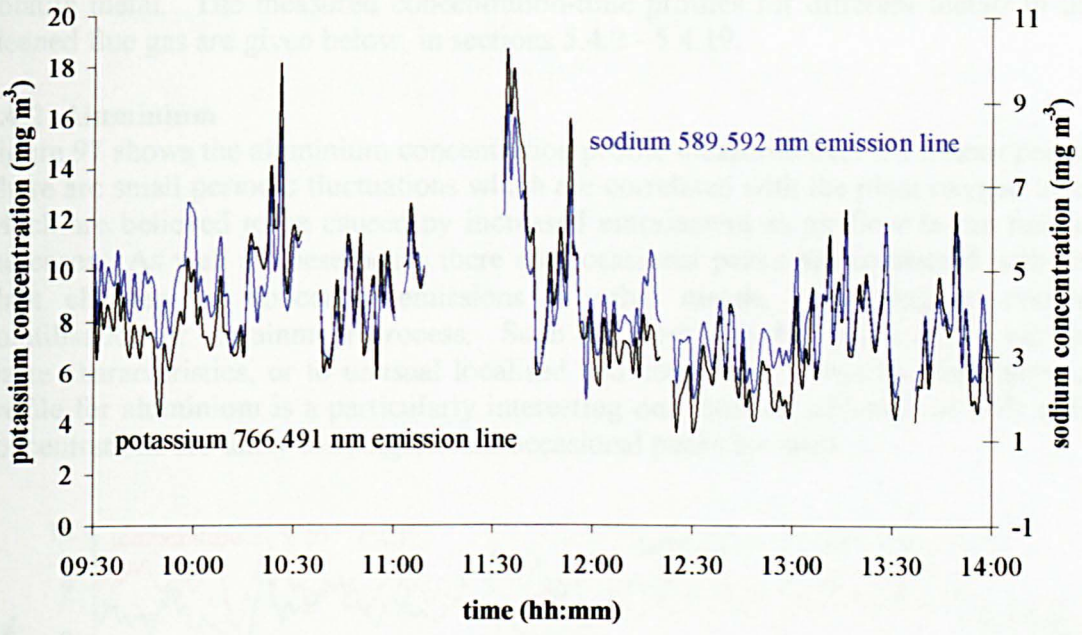


Figure 95: Comparison of sodium and potassium concentrations in un-cleaned flue gas from municipal waste incineration.

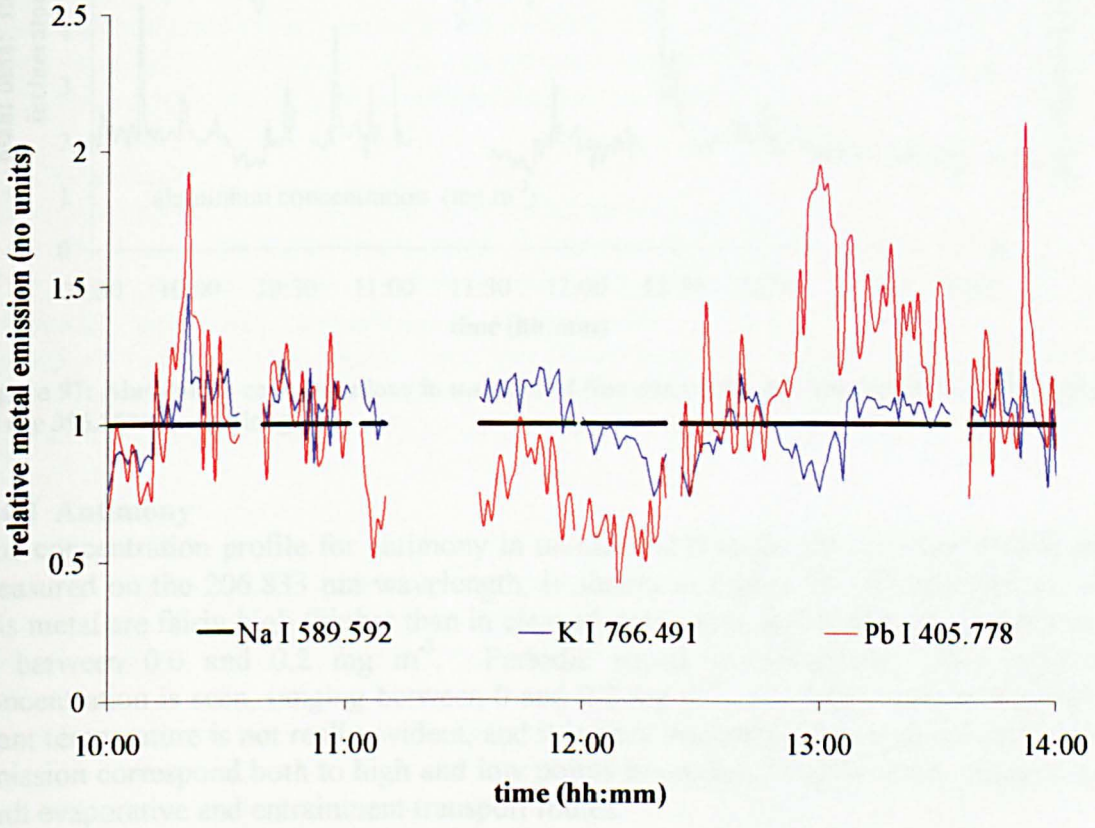


Figure 96: Relative emissions of potassium and lead normalised to the sodium emission profile.

Thus throughout the later examination of the emission profiles of different metals, the normalised sodium profile is used as a point of reference, indicating what "normal" metal emissions arise during those bulk furnace conditions, for an evenly distributed

volatile metal. The measured concentration-time profiles for different metals in un-cleaned flue gas are given below, in sections 5.4.2 - 5.4.19.

5.4.2 Aluminium

Figure 97 shows the aluminium concentration profile measured over a 4.5-hour period. There are small periodic fluctuations which are correlated with the plant oxygen level, which are believed to be caused by increased entrainment as air flow in the furnace increases. As well as these peaks there are occasional peaks not connected with any plant changes, or noticeable emissions of other metals, suggesting an unusual volatilisation or entrainment process. Such an event may be linked to the varying waste characteristics, or to unusual localised bed conditions. Thus the concentration profile for aluminium is a particularly interesting one, because although overall metal concentrations are fairly low, significant occasional peaks are seen.

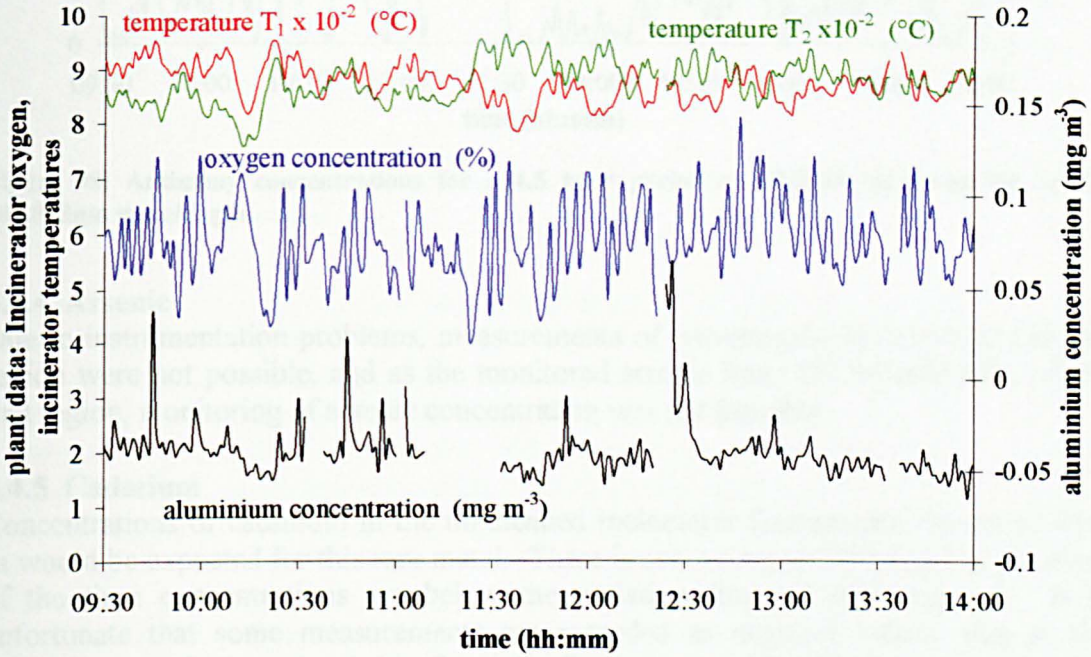


Figure 97: Aluminium concentrations in un-cleaned flue gas over a 4.5 hour period, as measured on the 396.152nm wavelength

5.4.3 Antimony

The concentration profile for antimony in un-cleaned flue gas for a 4 hour period, as measured on the 206.833 nm wavelength, is shown in Figure 98. Concentrations of this metal are fairly high (higher than in cleaned gas), given its low natural abundance, at between 0.0 and 0.2 mg m^{-3}. Periodic signal variation with plant oxygen concentration is seen, ranging between 0 and 0.2 mg m^{-3}. However, association with plant temperature is not really evident, and it is very interesting that peaks in antimony emission correspond both to high and low points in oxygen level, possibly suggesting both evaporative and entrainment transport routes.

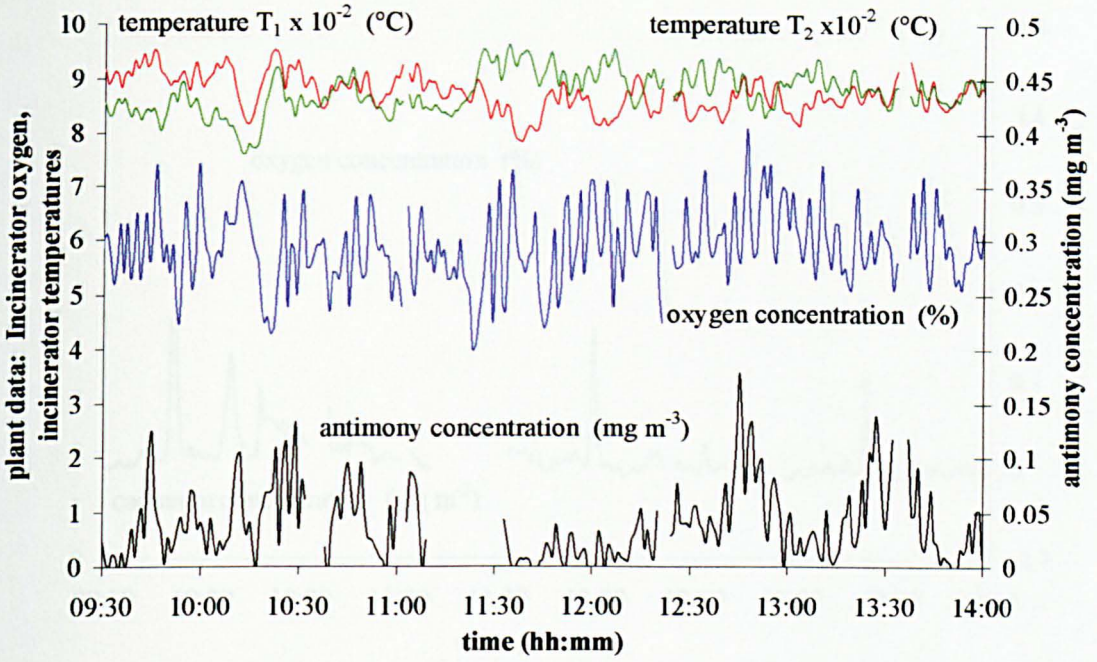


Figure 98: Antimony concentrations for a 4.5 hour period on 20/07/04 as measured on the 206.833nm wavelength

5.4.4 Arsenic

Due to instrumentation problems, measurements of wavelengths in the VUV spectral region were not possible, and as the monitored arsenic line (189.042nm) falls within that region, monitoring of arsenic concentration was not possible.

5.4.5 Cadmium

Concentrations of cadmium in the un-cleaned incinerator flue gas are extremely low, as would be expected for this rare metal. There is some temporal fluctuation, but most of the time concentrations are below the emission limit of 0.05 mg m^{-3}. It is unfortunate that some measurements are recorded as negative values, due to the calculation method used. Aside from the fluctuations with furnace oxygen (i.e. air flow) seen for several elements, the concentrations of cadmium are essentially stable, and effectively almost zero. Combustion chamber temperature has no discernible effect.

However, as seen in Figure 99, there are at a number of "emission events", where concentrations are over 0.1 mg m^{-3}, more than twice the typical baseline measurement, are recorded. There is no obvious association between these emission events with any particular plant conditions; some occur during high oxygen conditions, others during low oxygen periods. There is no clear correlation with furnace temperature: the emissions do not occur during particularly high furnace temperatures (though one may speculate that the peaks at 10:08 and 10:17 are in fact linked, and would form one continuous peak, had the temperature not fallen to an abnormally low level between these times). During some of the other measurement periods, other similar cadmium peaks are seen, though Figure 99 shows the most frequent and largest peaks. In some of the measured emission profiles, there are no significant peaks for cadmium, with the metal concentration essentially remaining at background level throughout the monitoring period.

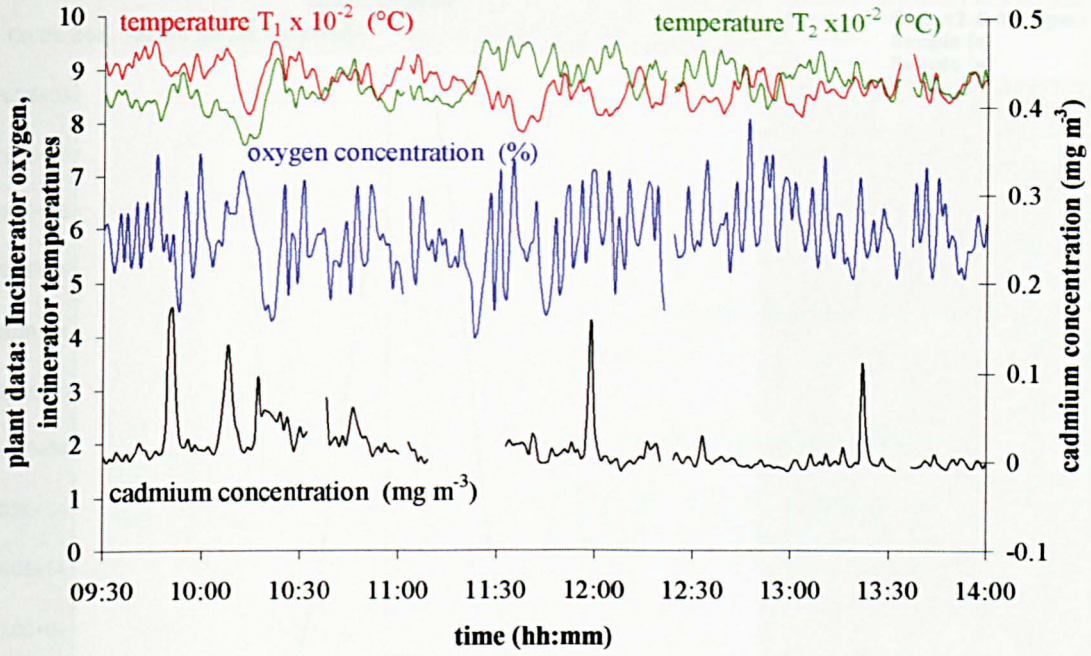


Figure 99: Cadmium concentrations in un-cleaned flue gas over a 4.5 hour period, as measured on the 226.503nm wavelength

Given the unusual and potentially significant results observed for cadmium, with most of the significant cadmium peaks seen during one morning of the four days of measurements, it was thought important to ensure that the signals observed were genuine. It was confirmed that the peaks seen on the Cadmium 226nm emission line were also seen on the 228.502 and 361.051nm lines, confirming the presence of cadmium. The spectral scans recorded were manually examined, to confirm that there was nothing unusual happening during the high cadmium emission events. Figure 100 shows a typical scan, with the blue line being a calibration scan with 0.1 ppm Cd (to indicate the presence of the line), the black line showing a typical flue cadmium measurement (a small background of Cd is seen), and the green line showing one of the largest flue cadmium emission events, which occurred on 20/07/04 at 09:50. Cadmium is clearly and unambiguously seen, with no realistic prospect of the signal having been caused by an interference or analytical method error, as the peak wavelength is exactly correct, and the emission is confirmed on multiple cadmium lines.

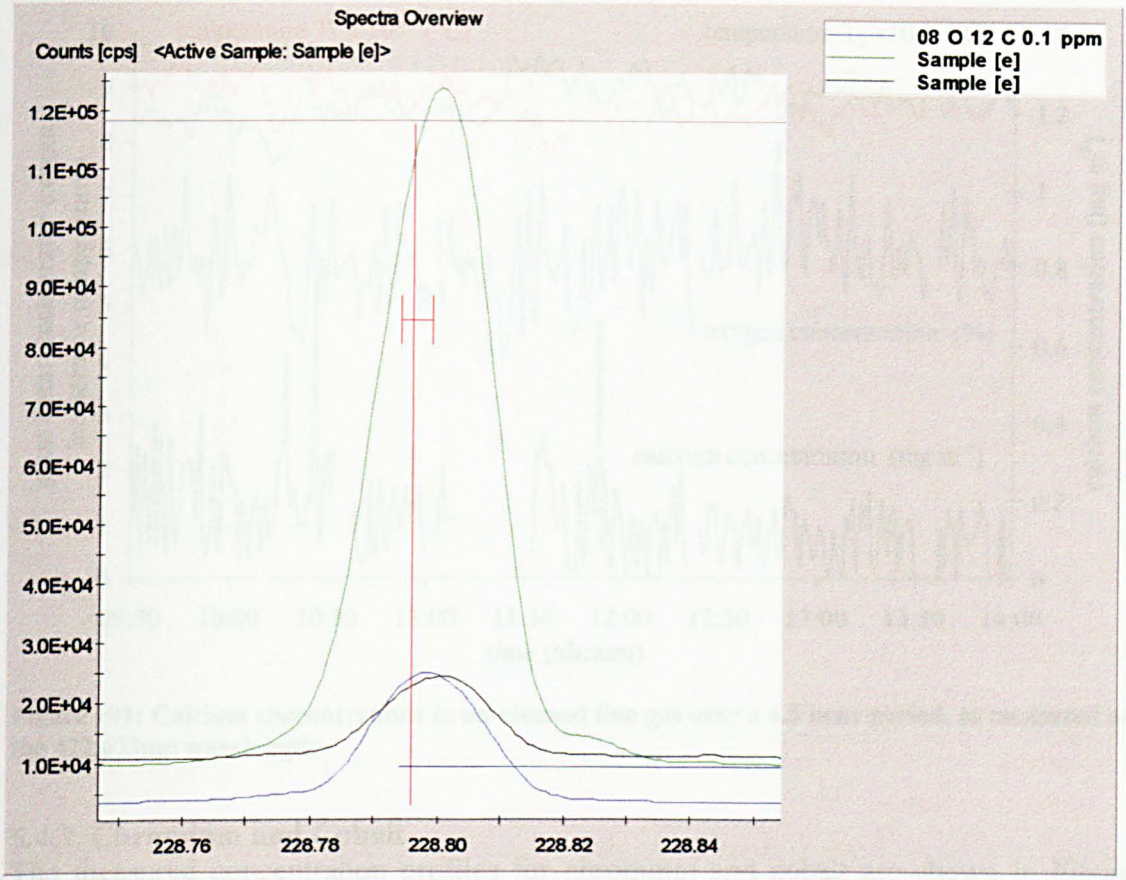


Figure 100: Emissions at the Cd 228.502nm wavelength during calibration, high cadmium emission, and normal cadmium emission in flue gas.

5.4.6 Calcium

The concentration profile for calcium is shown in Figure 101, as shown on the 422.673nm wavelength. The concentrations measured are fairly low; typically between 0.0 and 0.3 mg m^{-3}. The level of calcium in boiler residues tends to be high, but the low measured values here suggests that it is present as particles which are too large to reach the ICP readily. The association of calcium emission with oxygen level is strong, with high calcium nearly always being accompanied by high oxygen (though sometimes there is a slight time mismatch, due to the differing measurement periods on plant and in the lab), confirming theories of entrainment. In general, apart from the cycling with plant oxygen, there is less temporal variation in the calcium profile than for the volatile metals.

However, three peaks are seen on the profile, with calcium levels over 0.5 mg m^{-3}, at 10:17, 10:26, and 11:53.

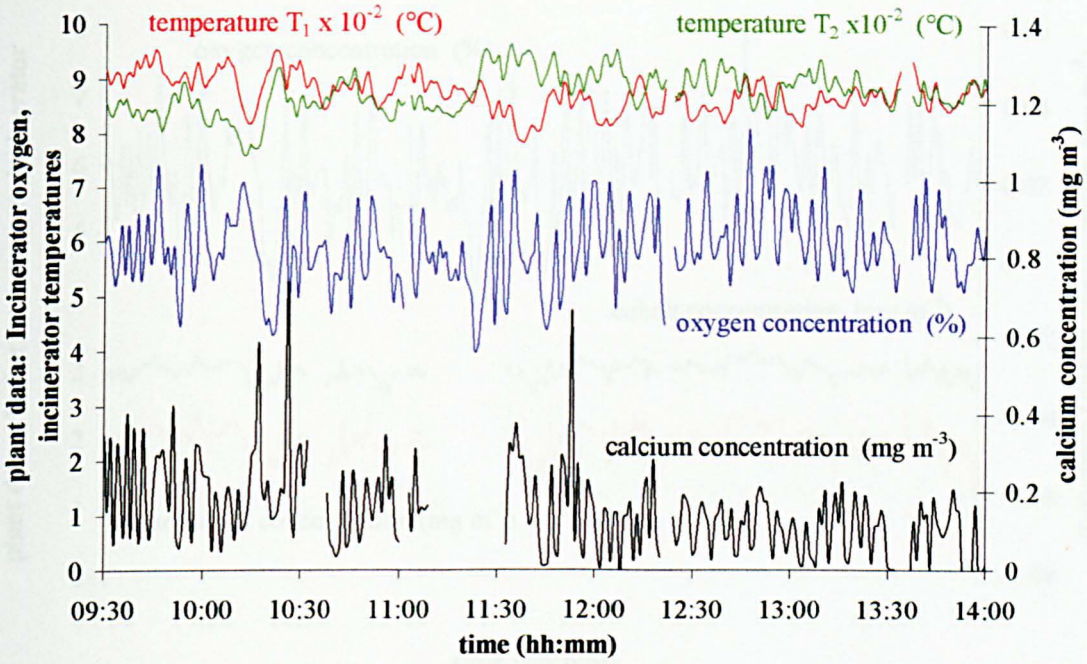


Figure 101: Calcium concentrations in un-cleaned flue gas over a 4.5 hour period, as measured on the 422.673nm wavelength

5.4.7 Chromium and Cobalt

The measured concentration profiles for chromium and cobalt are shown in Figure 102. Emissions are low (effectively zero, though recorded throughout as slightly negative), and approximately constant. The variation with time closely resembles the variation in plant oxygen (with a 1 minute time lag). It is therefore assumed that the variation observed is due to imperfect background correction for varying bulk gas composition, rather than actual emission variation, and in fact, there is effectively no cobalt in the gas stream at any point, in contrast with most metals examined.

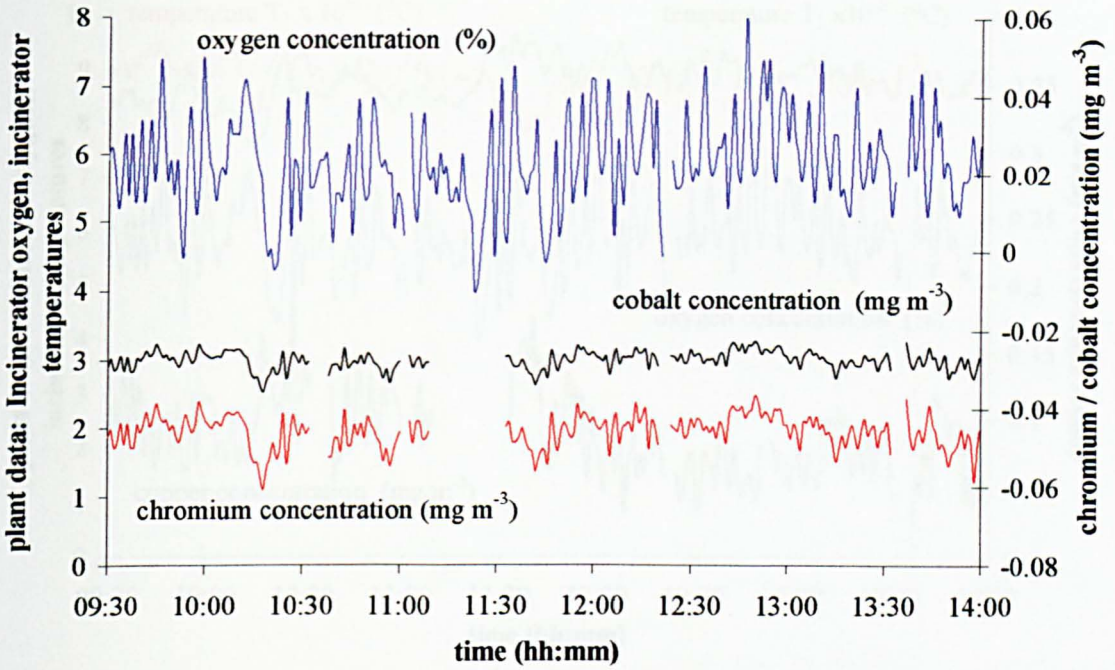


Figure 102: Cobalt and chromium concentrations in un-cleaned flue gas over 4.5 hour period, as measured on the 237.862nm and 283.563nm wavelengths respectively

Measured chromium emissions are low, and approximately constant. As with cobalt, the variation with time resembles the variation in plant oxygen, without significant exception. Once more it is assumed that the variation observed is due to imperfect background correction for the variation in bulk gas composition, rather than actual emission variation, and that chromium concentrations in the flue gas were effectively zero throughout. The close resemblance of the cobalt and chromium concentration profiles indicate how the observed variation is due more to background correction (zero-signal variation) than to changing metal concentrations.

5.4.8 Copper

The concentration profile for copper, as measured on the 324.754 nm emission line over a 4 hour period, is shown in Figure 103. Concentrations in the gas phase are fairly low, though there is significant temporal variation. Periodic variations are roughly correlated to plant oxygen level, with high copper concentration and high oxygen occurring together (with a slight time lag), implying entrainment. However, there is also limited association with temperature, with low temperatures tending to lead to low levels of copper in the gas phase.

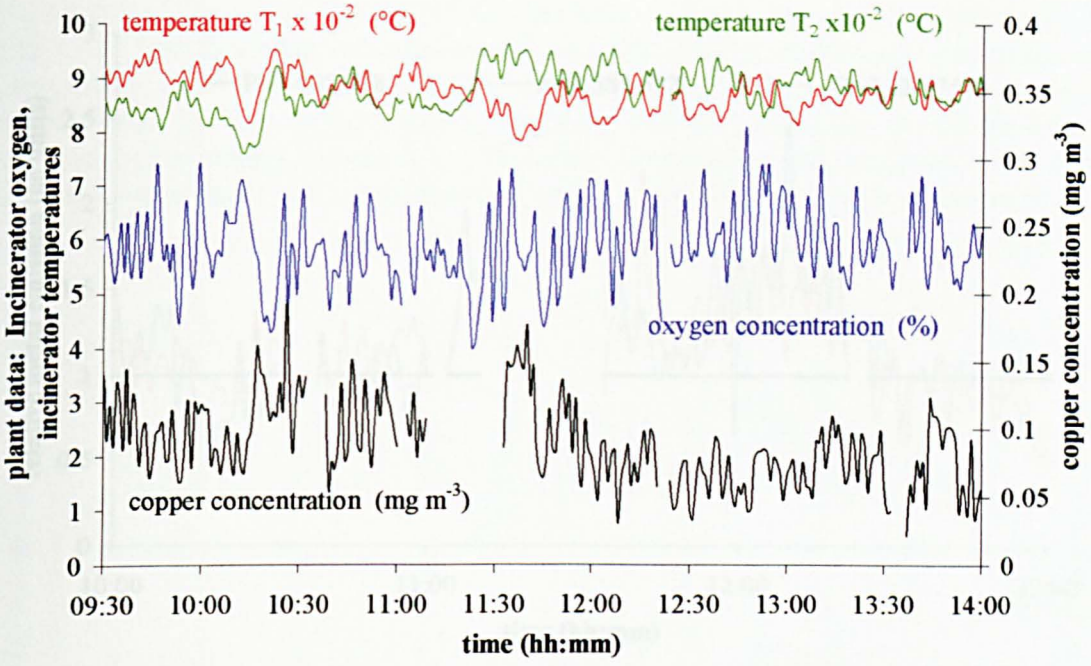


Figure 103: Copper concentrations in un-cleaned flue gas over a 4.5 hour period, as measured on the 324.754nm wavelength

Possibly the most interesting observation about the copper emission profile is the association with lead and sodium. As shown in Figure 104 - Figure 106, there is some (qualitative) link between lead and copper emissions (bearing in mind unusually high lead emissions between 12:30 and 13:00), and a clear link between sodium and copper emissions. However, the correlation between sodium and lead emissions is much weaker, suggesting that there is a causal link between copper and lead, and copper and sodium, but not directly between sodium and lead.

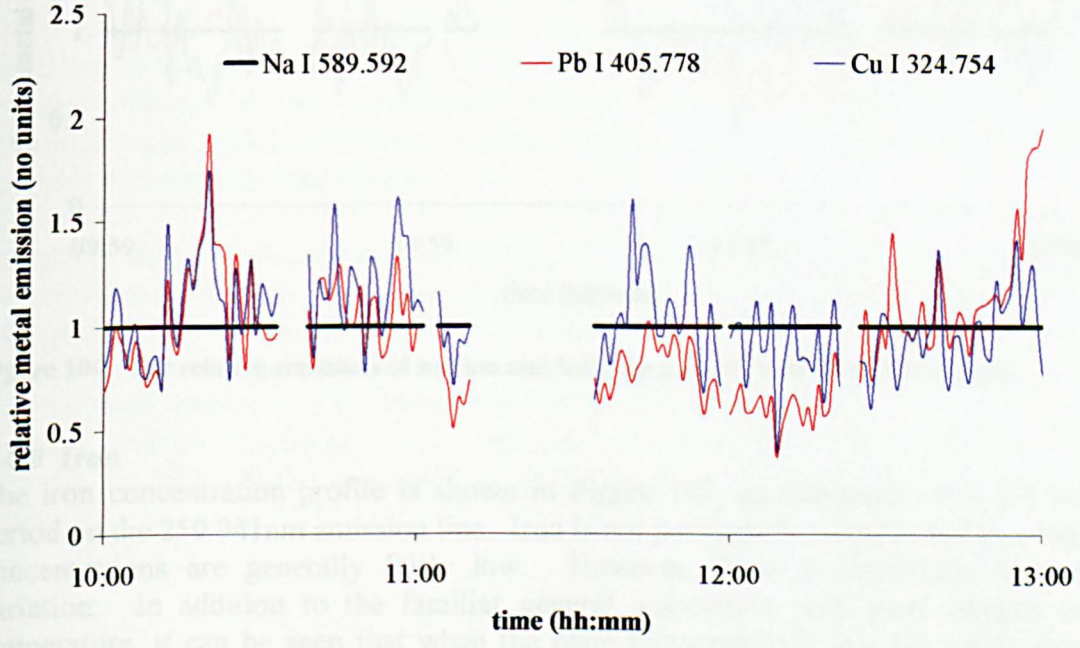


Figure 104: The relative emissions of lead and copper, normalised with respect to sodium

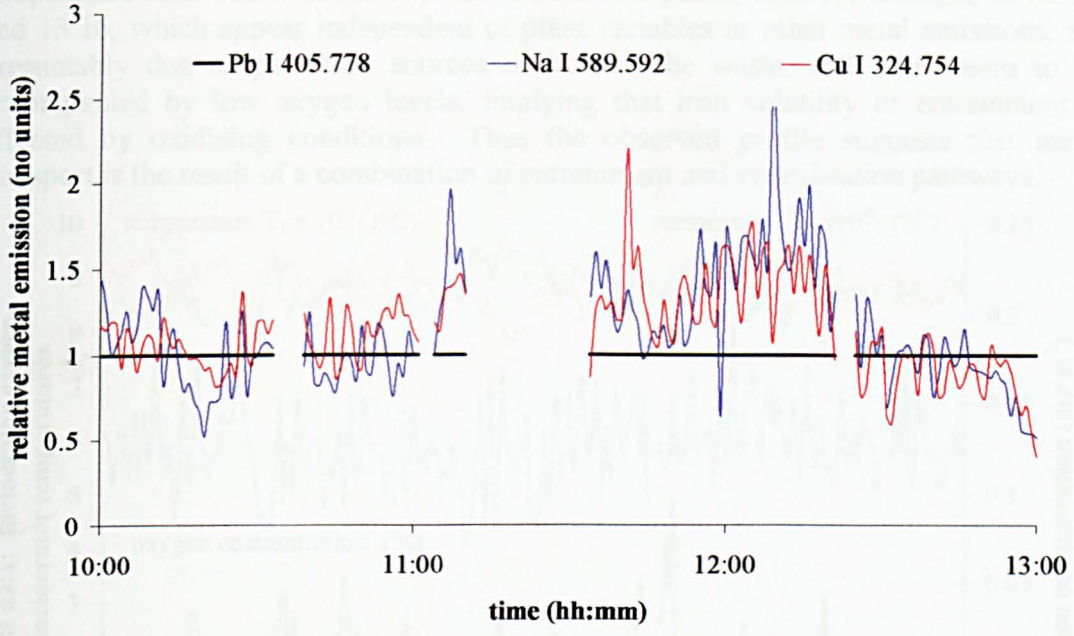


Figure 105: The relative emissions of sodium and copper, normalised with respect to lead

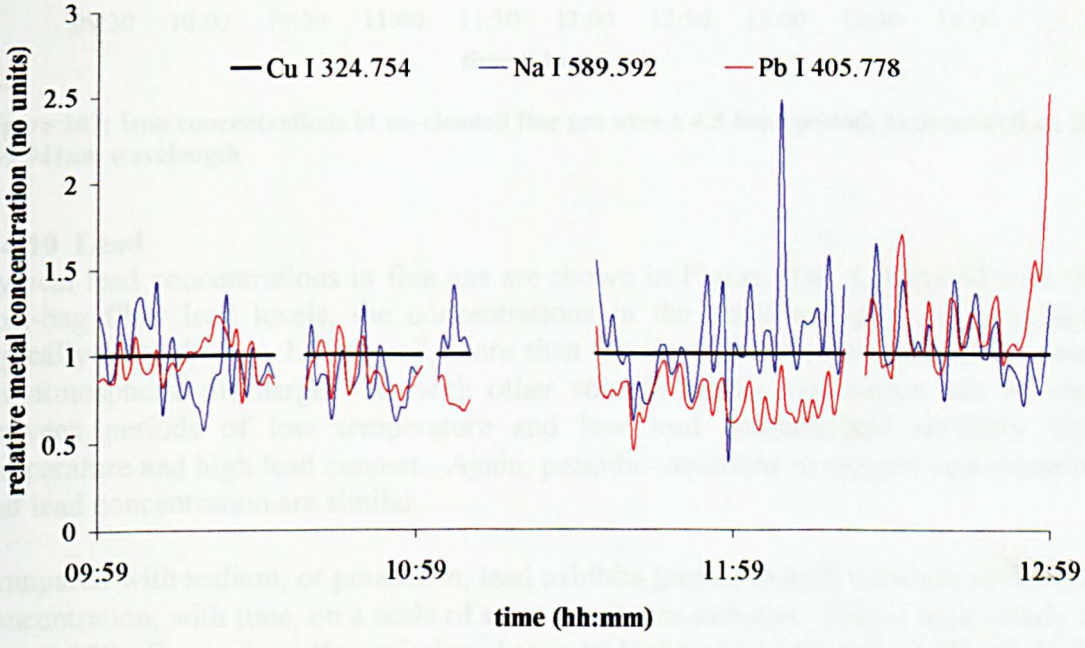


Figure 106: The relative emissions of sodium and lead, normalised with respect to copper

5.4.9 Iron

The iron concentration profile is shown in Figure 107, as measured for a 4.5 hour period on the 259.941nm emission line. Iron is not particularly volatile, and as a result concentrations are generally fairly low. However, there is significant temporal variation. In addition to the familiar general association with plant oxygen and temperature, it can be seen that when the plant temperature is low for a significant period on either thermocouple, and oxygen concentration is high, for example at 10:13, 11:44 and 13:00, iron emissions are low. The effect of temperature seems particularly high for iron, with emissions falling significantly when either thermocouple

temperature falls below about 850° C. Occasional peaks, seen for example at 12:28, and 13:16, which appear independent of plant variables or other metal emissions, are presumably due to particular sources of iron in the waste, and often seem to be accompanied by low oxygen levels, implying that iron volatility or entrainment is affected by oxidising conditions. Thus the observed profile suggests that metal transport is the result of a combination of entrainment and volatilisation pathways.

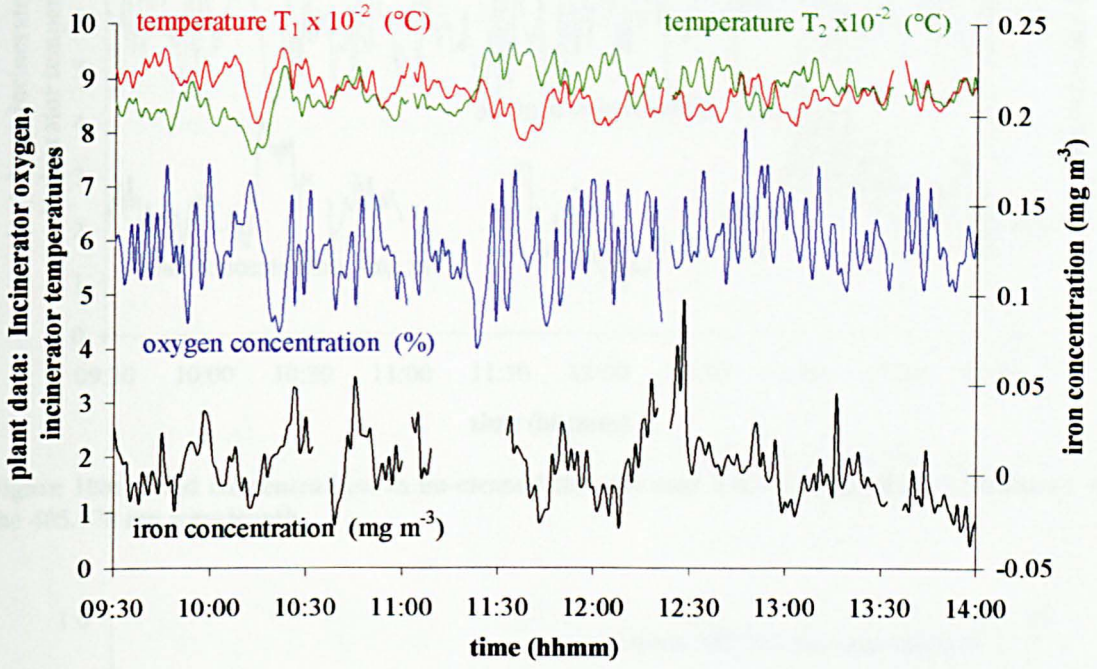


Figure 107: Iron concentrations in un-cleaned flue gas over a 4.5 hour period, as measured on the 259.941nm wavelength

5.4.10 Lead

Typical lead concentrations in flue gas are shown in Figure 108. Compared with the post-bag filter lead levels, the concentrations in the uncleaned gas are very high, typically around 0.5 – 1.0 mg m^{-3}, more than ten times the maximum emission level for atmospheric discharge. As with other volatile metals, correlation can be seen between periods of low temperature and low lead content, and similarly high temperature and high lead content. Again, periodic variations in oxygen concentration and lead concentration are similar.

Compared with sodium, or potassium, lead exhibits greater overall variation in flue gas concentration, with time, on a scale of several minutes to hours. This is seen clearly in Figure 109. For sodium, the emissions between 10:00 and 11:00 and 12:30 and 13:00 overlay well with lead emissions, despite their different relative magnitudes. In contrast, lead emissions are noticeably relatively increased between 13:00 and 13:30, whereas between 12:00 and 12:15, concentrations of lead are particularly low. By contrast, the concentration of sodium or potassium during these four regions is broadly similar.

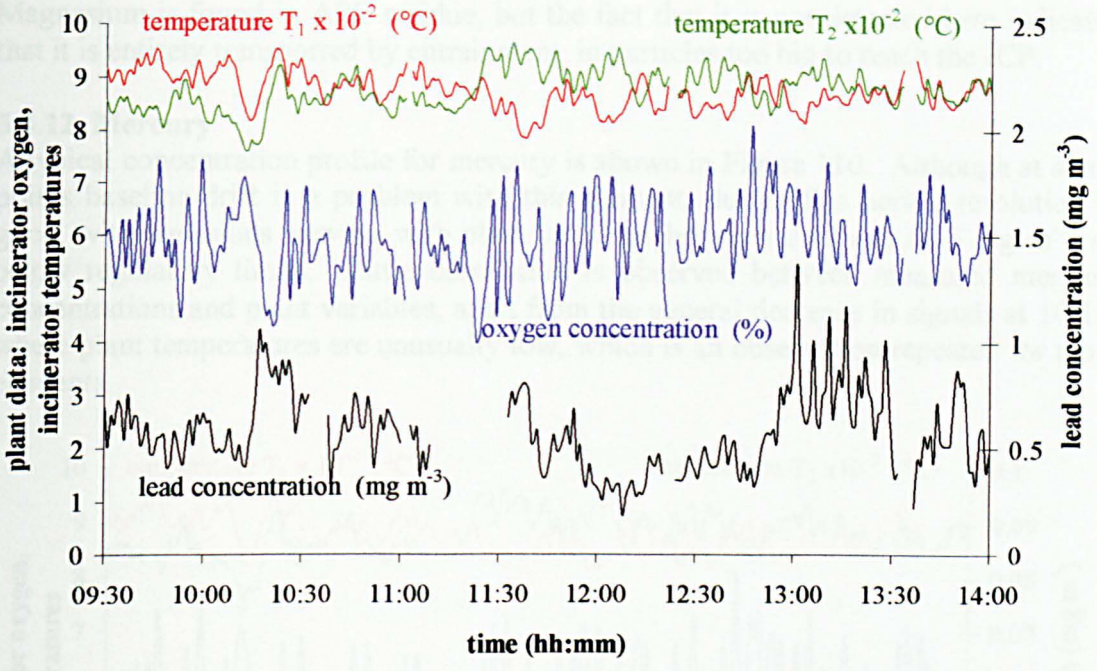


Figure 108: Lead concentrations in un-cleaned flue gas over a 4.5 hour period, as measured on the 405.778 nm wavelength

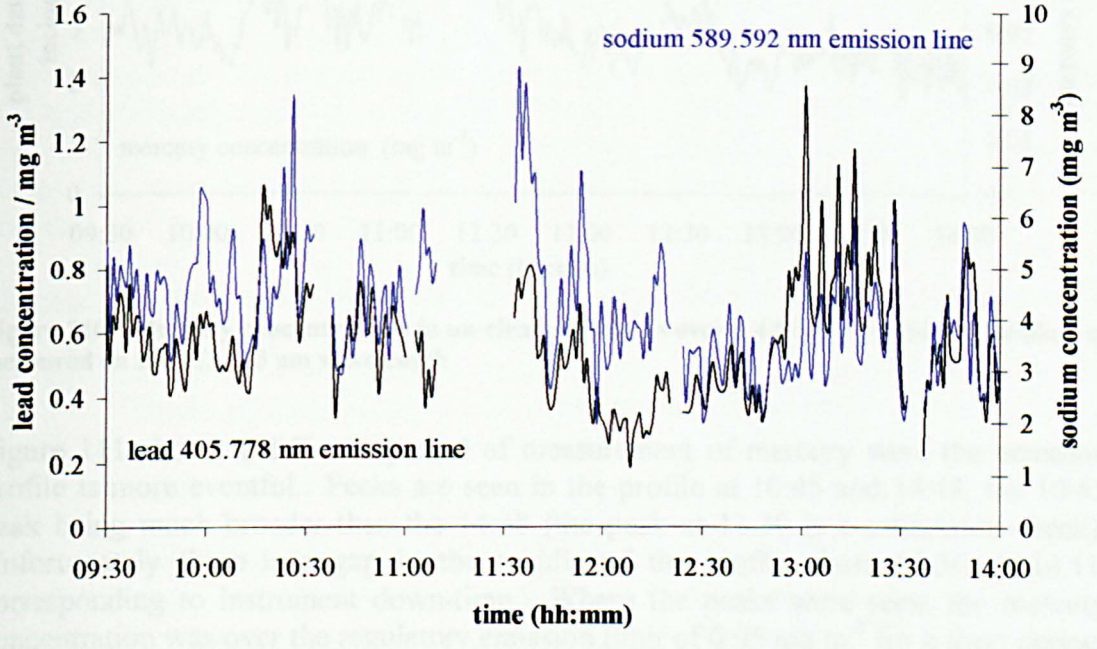


Figure 109: Comparison of sodium and lead concentrations for a 4.5 hour period, showing incomplete correlation

5.4.11 Magnesium and Manganese

The magnesium and manganese concentrations measured in the flue gas fluctuate around zero throughout, with variation observed exactly matching the plant oxygen fluctuation. The manganese profile shows negative measured concentrations throughout measurement, due to imperfect calibration matrix matching, but essentially corresponds to a zero signal. Therefore concentration profiles are not shown, as it is essentially the same as those shown for cobalt and chromium (section 5.4.7).

Magnesium is found in APC residue, but the fact that it is not detected here indicates that it is entirely transported by entrainment, in particles too big to reach the ICP.

5.4.12 Mercury

A typical concentration profile for mercury is shown in Figure 110. Although at some points baseline drift is a problem with this element, during this period resolution is good, with emissions varying with plant variables between 0.02 and 0.05 mg m^{-3}, so below regulatory limits. Little correlation is observed between measured mercury concentrations and plant variables, apart from the general decrease in signals at 10.15, where plant temperatures are unusually low, which is an observation repeated for most elements.

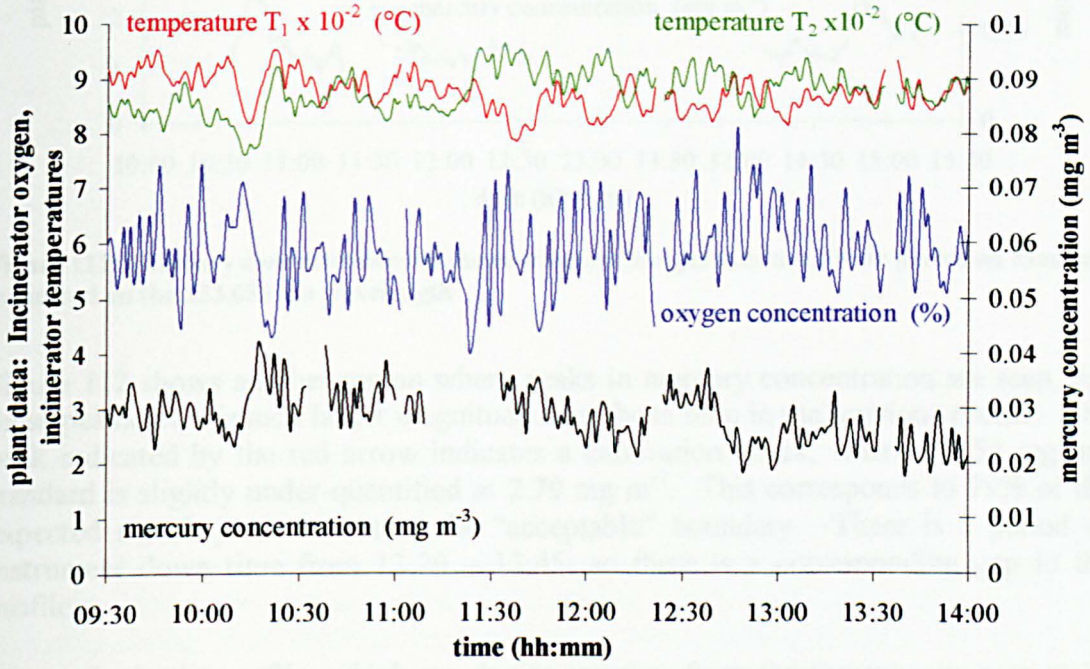


Figure 110: Mercury concentrations in un-cleaned flue gas over a 4.5 hour period on Tuesday, as measured on the 253.653 nm wavelength

Figure 111 shows a different period of measurement of mercury were the emission profile is more eventful. Peaks are seen in the profile at 10:45 and 14:48, the 10:45 peak being much broader than the 14:48 (the peak at 11.30 is a calibration check). Unfortunately there is a gap in the middle of the profile, from 12.36 to 14.11, corresponding to instrument down-time. Where the peaks were seen, the mercury concentration was over the regulatory emission limit of 0.05 mg m^{-3} for a short period. These peaks are confirmed on the 194.236nm line, and are not noticeably associated with any other process or emission events. This is to be expected, as mercury is predicted (by thermodynamics) to be fully volatilised in any normal plant operating conditions.

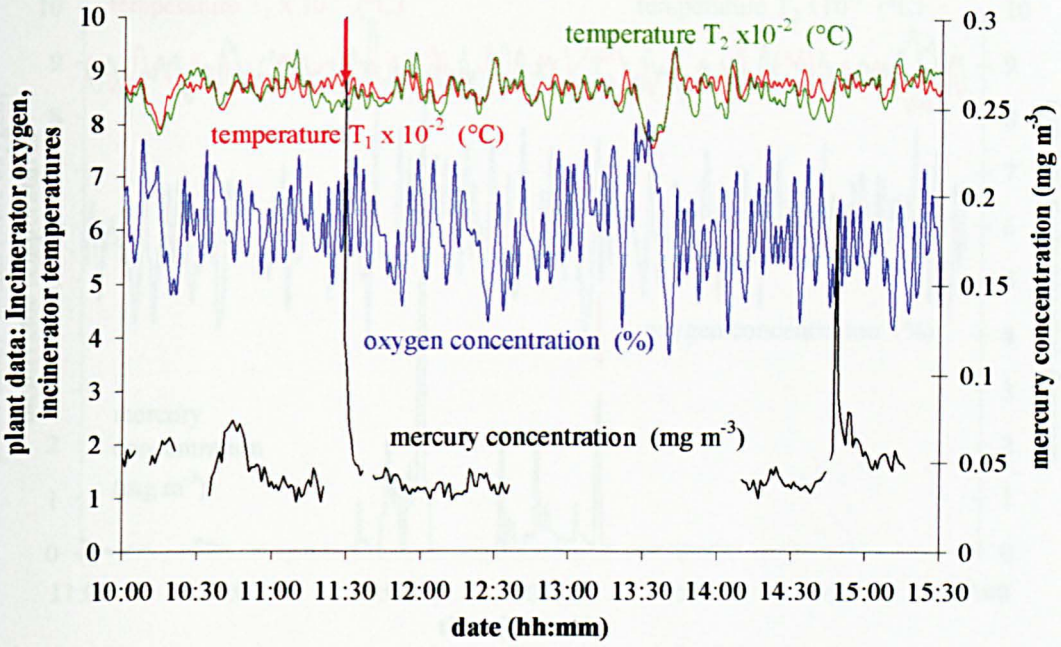


Figure 111: Mercury concentrations in the un-cleaned flue gas over a 4.5 hour period on Monday, measured on the 253.653 nm wavelength

Figure 112 shows another region where peaks in mercury concentration are seen, but these peaks are of much larger magnitude than those seen in the previous profile. The peak indicated by the red arrow indicates a calibration check, where a 3.54 mg m^{-3} standard is slightly under-quantified at 2.79 mg m^{-3}. This corresponds to 79% of the expected signal, just 1% out of the "acceptable" boundary. There is a period of instrument down time from 13:20 – 13:45, so there is a corresponding gap in the profile.

The peaks in the profile, which are due to mercury from the furnace, are seen to be extremely large – larger than the calibration check - giving high concentrations of mercury in the pre-clean-up flue gas for about 2 hours, with significant peaks within that time. The largest peak concentrations for mercury were almost as large as those for sodium or potassium, the most concentrated metals in the waste stream monitored. Such a result was highly unexpected.

Given the unexpectedly high concentrations observed in this period, a careful cross-checking process was completed, to ensure that these figures were actually due to mercury, and were appropriately quantified. Firstly, reasonable quantification of the calibration check at 2:27 was confirmed, as detailed above. Secondly, the peaks were confirmed on the 194.236nm and 435.832 nm lines, where measured values were found to be similar, with the 435 nm line only being sensitive enough to show these larger peaks, and not some of the smaller ones shown previously.

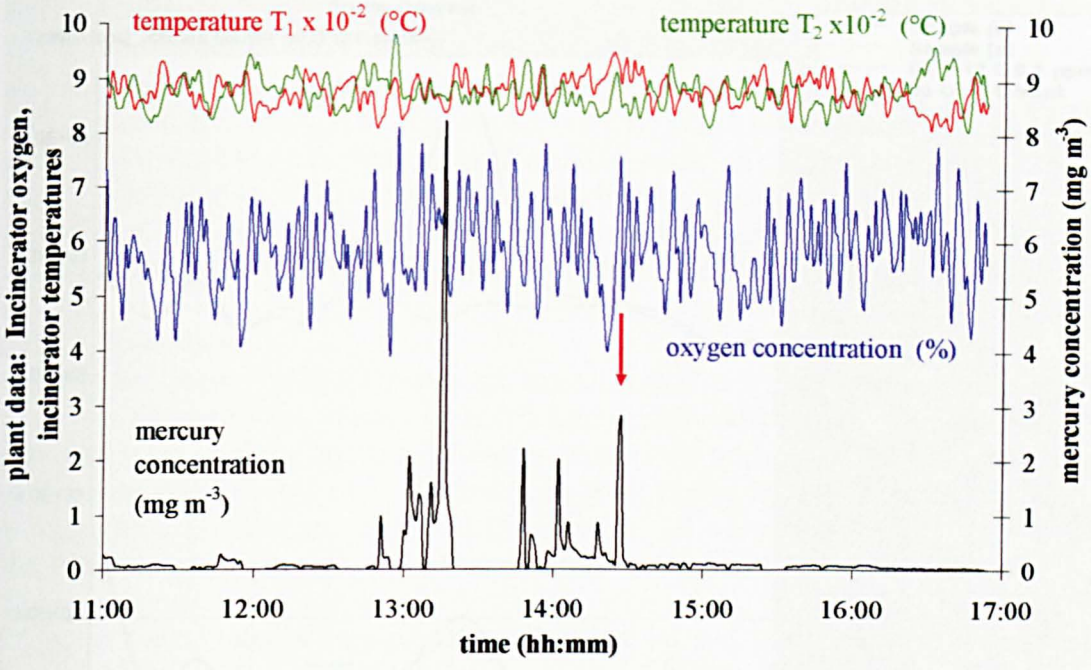


Figure 112: Mercury concentrations for a 6 hour period on Wednesday, as measured on the 253.653 nm wavelength

Finally, the emission scans of wavelengths near mercury monitor lines were checked, to ensure that measured signals were in fact due to mercury. Figure 113 and Figure 114 show typical scans where signals are seen. Green scan is laboratory calibration blank, black is laboratory calibration 0.1ppm standard, each in matrix of 12% CO_2, 8% O_2 calibration gas. Dark green scan is a flue gas which is approximately blank in Hg, and the blue line is flue gas with high recorded Hg value measured at 14:47 on 19/07/04. Although the scans shown were not the largest peaks seen during the week, the scans during those highest mercury signals were similar (except in magnitude of the measured flue signal), and confirmed that the results were clearly and unambiguously due to mercury from the furnace. Evidence is seen of the shifting spectrum background between the calibration and test conditions, but it is also seen that careful background correction mitigates that potential problem.

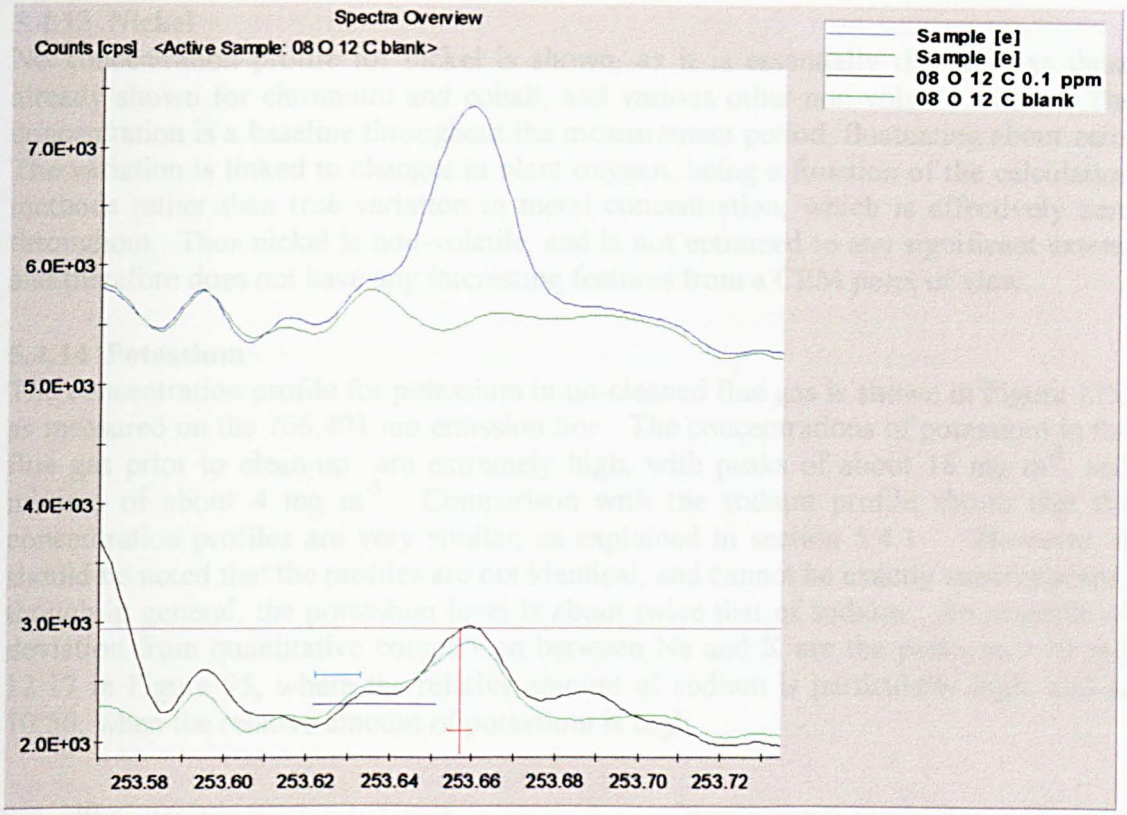


Figure 113: Emissions at the Hg 253.653 nm wavelength during calibration, high mercury emission, and normal mercury emission in flue gas.

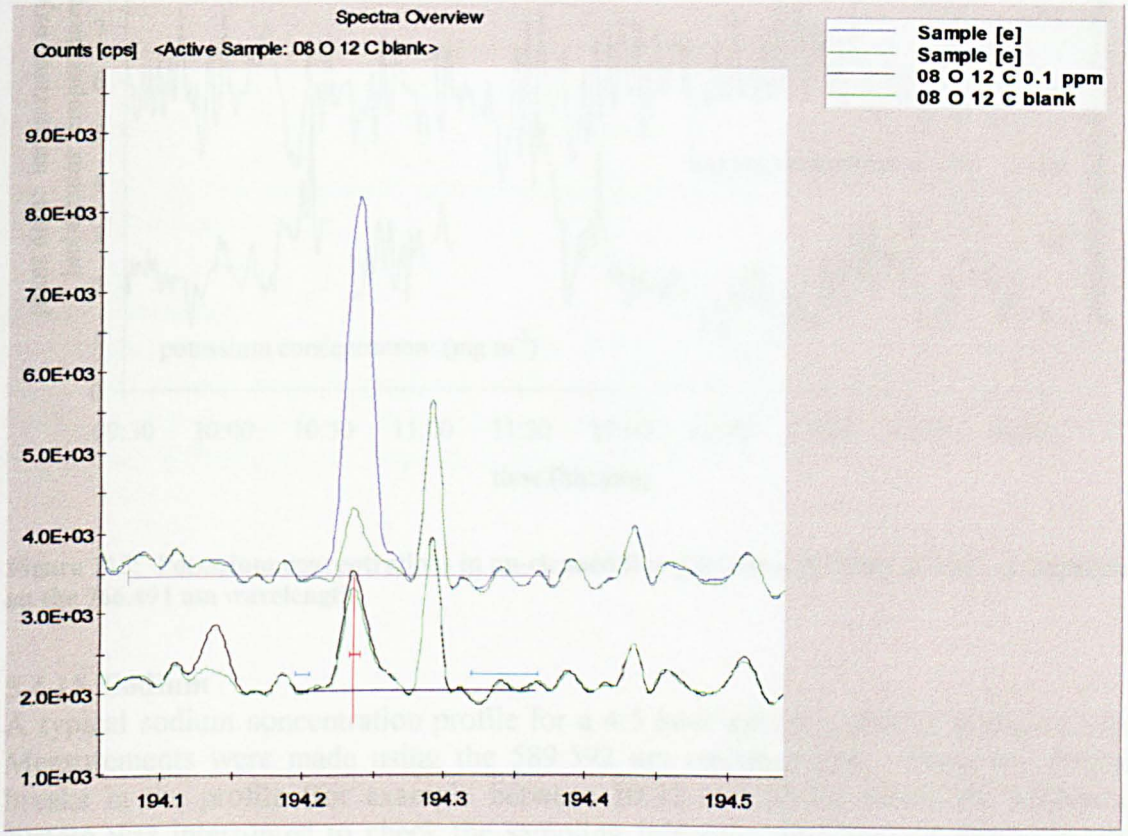


Figure 114: Emissions at the 194.236nm wavelength during calibration, high cadmium emission, and normal cadmium emission in flue gas.

5.4.13 Nickel

No concentration profile for nickel is shown, as it is essentially the same as those already shown for chromium and cobalt, and various other non-volatile metals. The concentration is a baseline throughout the measurement period, fluctuating about zero. The variation is linked to changes in plant oxygen, being a function of the calculation methods rather than true variation in metal concentration, which is effectively zero throughout. Thus nickel is non-volatile, and is not entrained to any significant extent, and therefore does not have any interesting features from a CEM point of view.

5.4.14 Potassium

The concentration profile for potassium in un-cleaned flue gas is shown in Figure 115, as measured on the 766.491 nm emission line. The concentrations of potassium in the flue gas prior to clean-up are extremely high, with peaks of about 18 mg m^{-3}, and minima of about 4 mg m^{-3}. Comparison with the sodium profile shows that the concentration profiles are very similar, as explained in section 5.4.1 . However, it should be noted that the profiles are not identical, and cannot be exactly superimposed; though in general, the potassium level is about twice that of sodium. An example of deviation from quantitative comparison between Na and K are the peaks at 9:59 and 12:17 in Figure 95, where the relative amount of sodium is particularly high, and at 10:50, when the relative amount of potassium is high.

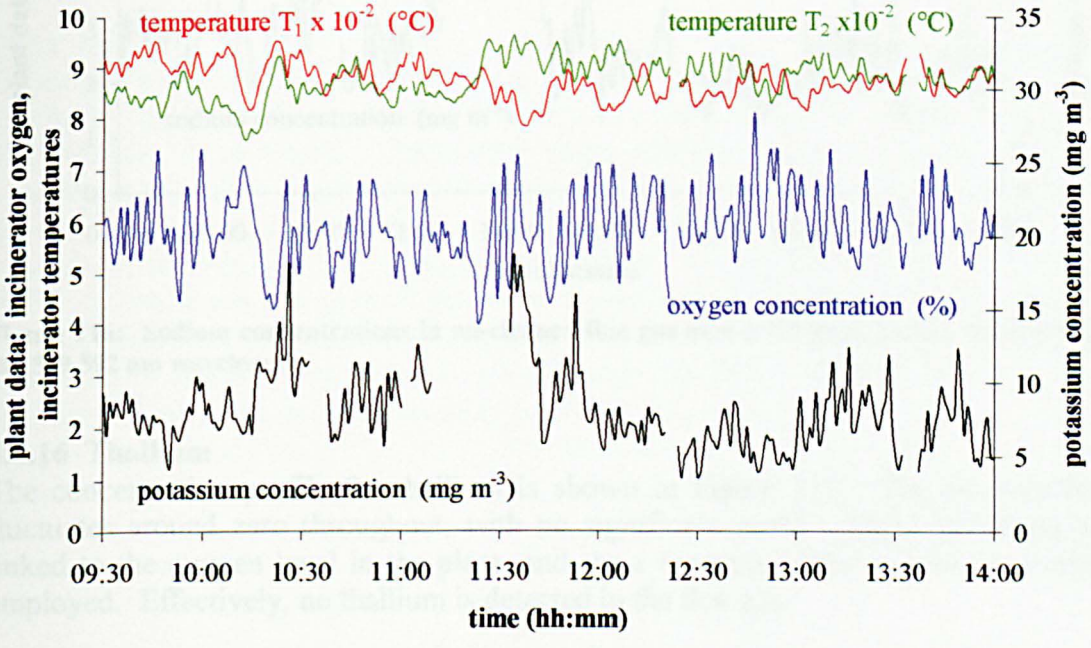


Figure 115: Potassium concentrations in un-cleaned flue gas over a 4.5 hour period, as measured on the 766.491 nm wavelength

5.4.15 Sodium

A typical sodium concentration profile for a 4.5 hour period is shown in Figure 116. Measurements were made using the 589.592 nm emission line. There are several breaks in the profile (for example between 10:32 and 10:38) where the analytical system was interrupted to check the sampling integrity. Sodium concentrations are characteristically high, typically between 2 and 8 mg m^{-3}, which is in good agreement with the high concentrations of this volatile metal found in APC residues.

There is evident correlation between sodium emissions and both furnace oxygen and temperature, with low temperature and sodium emission generally going together. Typically, the correlation of temperature with sodium can be seen most clearly when both thermocouple measurements are low, and sodium concentrations are correspondingly low. As the temperature rises again, the concentrations of sodium increase once more. Such a motif is most clearly seen at about 10:20 – 10:30. Correlation with plant oxygen is clearly visible, with general variations in sodium and oxygen having approximately the same period, of about 3-5 minutes between peaks. However, this association is neither quantitative nor exactly temporally co-ordinated; generally sodium emissions correspond to, or follow, high oxygen levels.

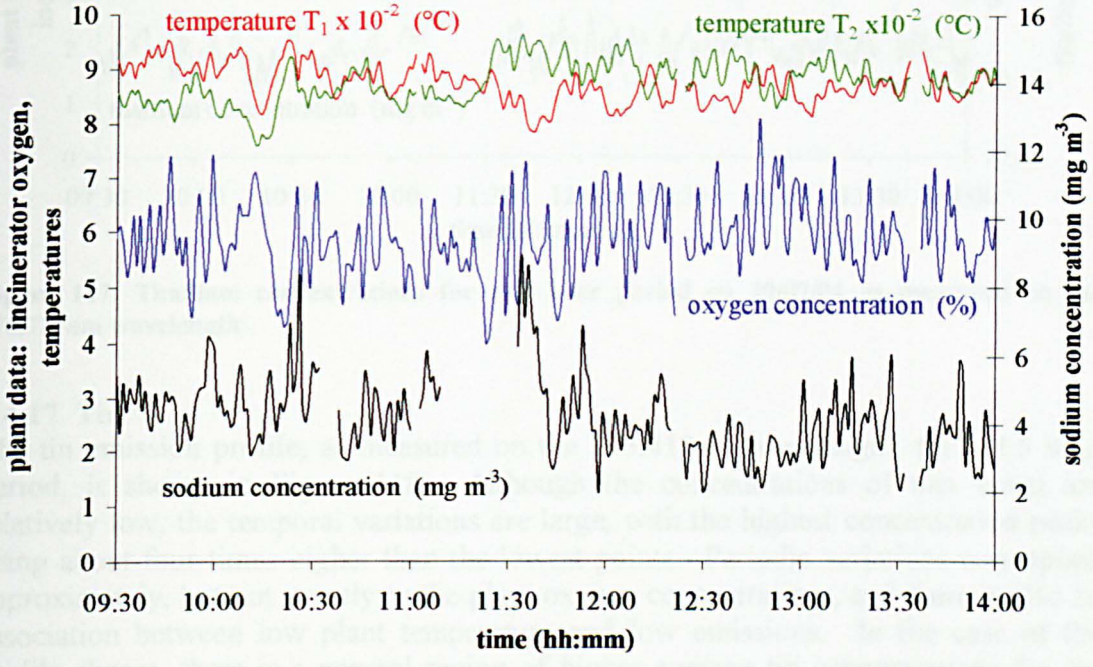


Figure 116: Sodium concentrations in un-cleaned flue gas over a 4.5 hour period, measured on the 589.592 nm wavelength

5.4.16 Thallium

The concentration profile for thallium is shown in Figure 117. The concentration fluctuates around zero throughout, with no significant peaks. Slight variations are linked to the oxygen level in the plant, and are a function of the calculation method employed. Effectively, no thallium is detected in the flue gas.

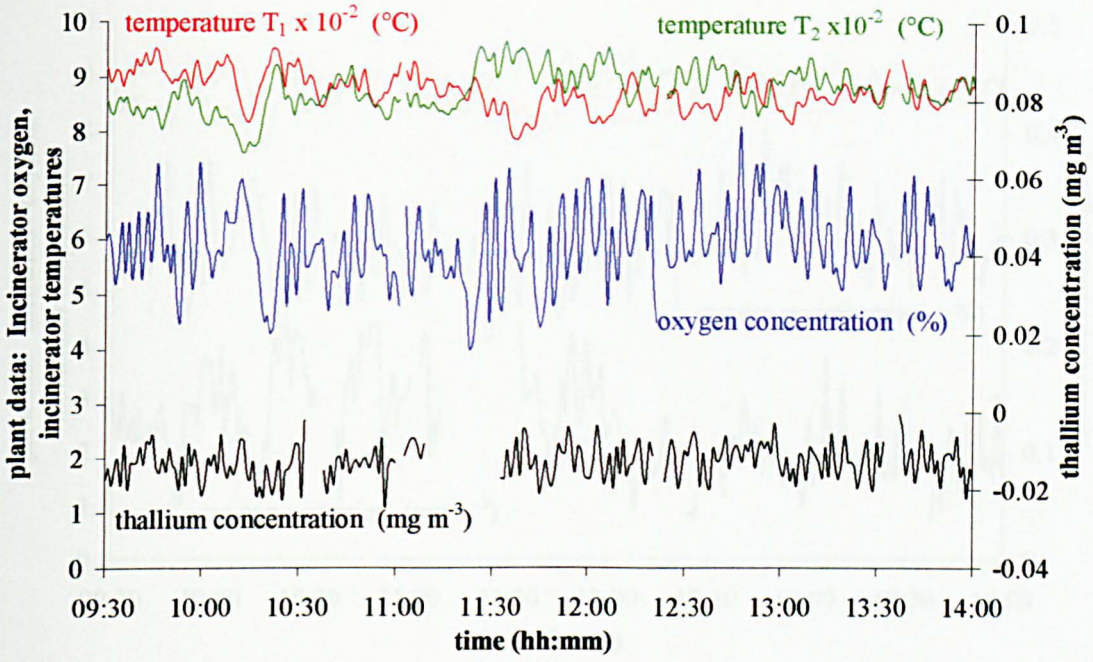


Figure 117: Thallium concentrations for a 4 hour period on 20/07/04 as measured on the 276.787nm wavelength

5.4.17 Tin

The tin emission profile, as measured on the 303.412nm wavelength, for a 4.5 hour period, is shown in Figure 118. Although the concentrations of this metal are relatively low, the temporal variations are large, with the highest concentration peaks being about four times higher than the lowest points. Periodic variations correspond approximately, but not exactly to the plant oxygen concentrations, and there is also an association between low plant temperature and low emissions. In the case of the profile shown, there is a general region of higher average tin concentrations for the first 1.5 hours shown, and lower average tin concentrations for the last 1.5 hours, with a changeover period between. It is assumed that this variation is due to the "availability" of tin in the waste stream.

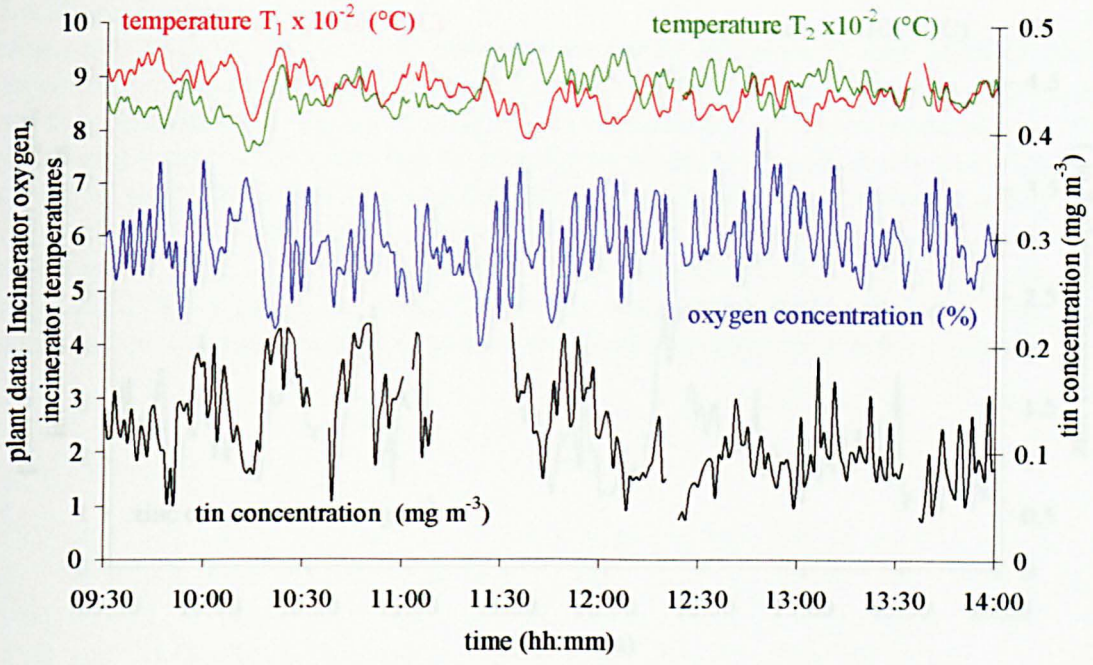


Figure 118: Tin concentrations in un-cleaned flue gas over a 4.5 hour period, as measured on the 303.412 nm wavelength

5.4.18 Vanadium

The concentration profile for vanadium is not shown. The variations in concentration correspond to the plant oxygen levels, and are merely a function of the calculation method; the profiles being near-identical to those for nickel, chromium and cobalt.. Thus the measured vanadium levels are approximately constant, and despite a slight background correction error, are effectively zero.

5.4.19 Zinc

The concentration profile for zinc is shown in Figure 119, as measured on the 213.856 nm emission line. The Zn 202.548 nm profile is almost identical, with minimal variation in quantification between the two lines, indicating good analytical precision. Periodic fluctuations are seen, which correspond somewhat to the fluctuations in plant conditions, with concentrations varying between about 0.5 mg m^{-3} and 2.5 mg m^{-3}.

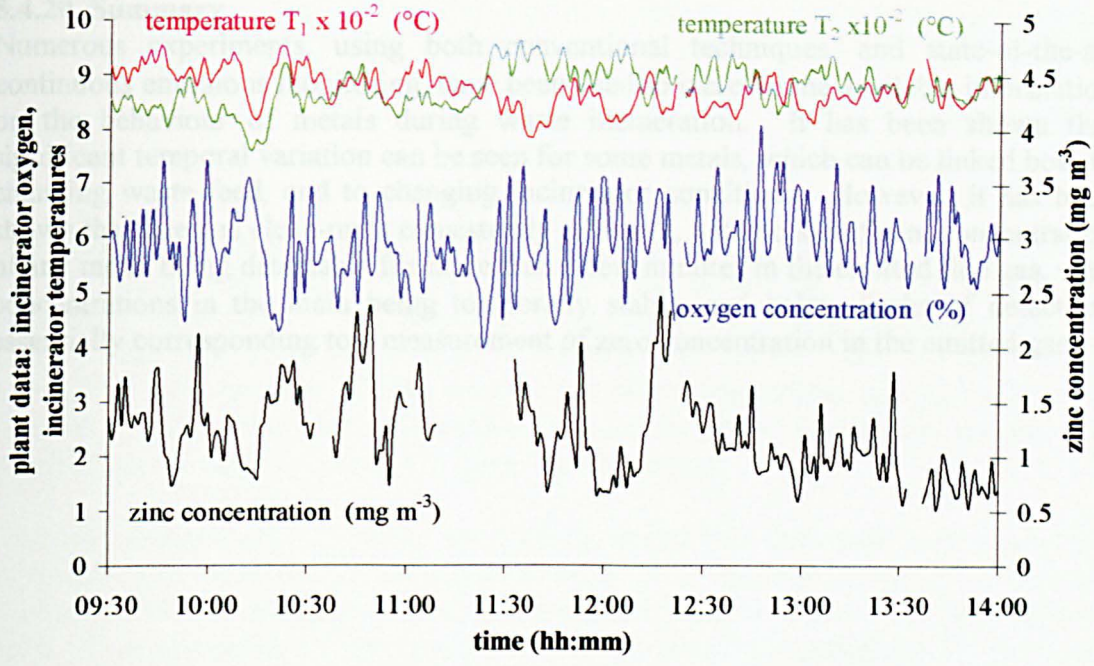


Figure 119: Zinc concentrations in un-cleaned flue gas over a 4.5 hour period, as measured on the 213.856 nm line

Figure 120 shows a comparison between the relative concentrations of zinc and sodium, and it is once more seen that general correlation between the concentrations of the two metals is good, particularly for example between 09:30 and 10:30, and again between 13:00 and 14:00. This comparison emphasises the independence of the zinc peaks at 10:40-10:50 and 12:15-12:30 from the emissions of other metals, reinforcing the supposition that they are a result of changing waste feed, rather than plant conditions.

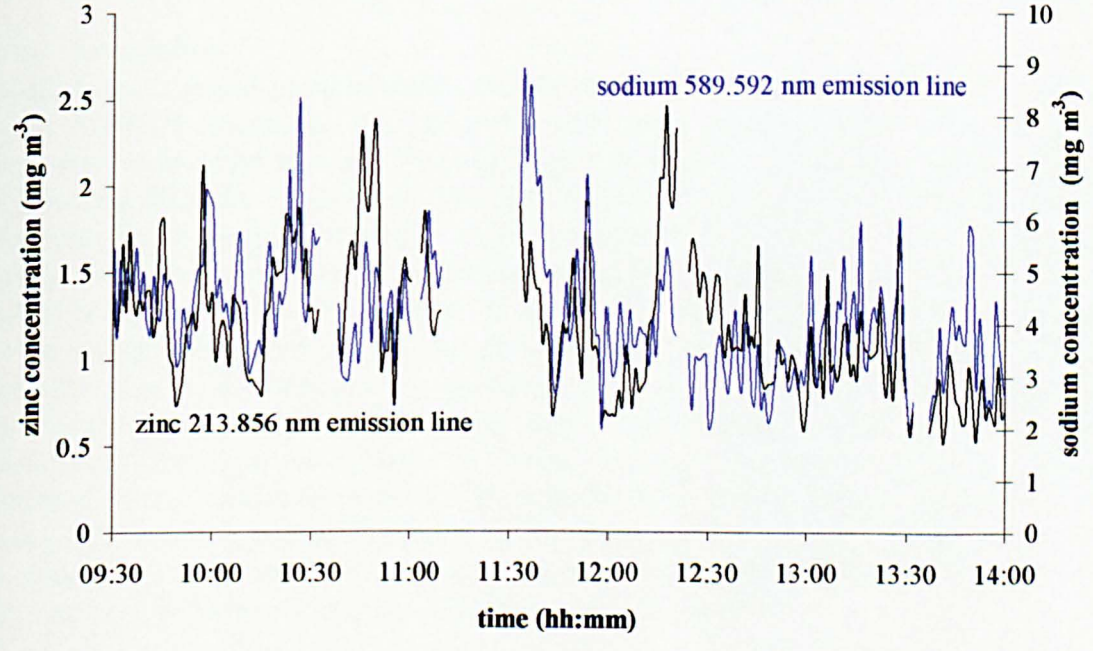


Figure 120: Comparison of sodium and zinc concentrations for a 4.5 hour period.

5.4.20 Summary

Numerous experiments, using both conventional techniques, and state-of-the-art continuous emissions monitoring, have been used to increase the available information on the behaviour of metals during waste incineration. It has been shown that significant temporal variation can be seen for some metals, which can be linked both to changing waste feed, and to changing incinerator conditions. However, it has been shown that flue gas clean-up is consistently effective, with no significant concentration of any metal being detectable for more than a few minutes in the emitted flue gas, with concentrations in the main being temporally stable, and below limits of detection, essentially corresponding to a measurement of zero concentration in the emitted gas.

Chapter Six:

Discussion

The following section combines information obtained on the behaviour of different metals during waste incineration, obtained from a number of experiments and theoretical predictions. The results of continuous monitoring of cleaned and un-cleaned flue gas from a full-scale incinerator, the results from municipal waste incinerator solid residues, and the results from laboratory furnace spiking experiments together show how metals partition during incineration, how volatile they are, and how much temporal variation there is in metal concentrations.

The data obtained experimentally has been compared with thermodynamic predictions of metal behaviour during incineration, with good agreement (given the known limitations of each technique, discussed in chapter 5 and 4 respectively), and thus the level of understanding of the processes involved in metal partitioning has increased substantially. Overall, the predictions are in excellent general agreement with experimental data, and the improved treatment of slags in these calculations make predictions considerably more accurate than in earlier thermodynamic studies where volatility tended to be significantly over-predicted, due to the inability to fully consider non-volatile slag products. For some metals, it is seen that there is a link between the concentration of that metal and another; for others, the concentration can be linked to other combustion conditions. For some, the variation is not fully proven, but appears to be related to variations in the waste feed, in some cases corresponding to the combustion of specific metal-containing items. The overall findings for the behaviour of each metal during combustion are given individually, drawing on information from throughout Chapter 4 on thermodynamic predictions, and Chapter 5, the results of experimental studies.

6.1.1 Aluminium

Aluminium is found in significant quantity in both the bottom ash and APC residue from MSW incineration, the concentrations being approximately equal in each. However, aluminium was not found in large concentration in the un-cleaned flue gas, confirming that the majority of this metal found in the fly ash is transported by entrainment, in particles too large to be sampled by the CEML. Occasional small spikes were seen, nevertheless, in the un-cleaned flue gas profile, though no significant spikes were seen in the cleaned gas. It is not clear whether these spikes were caused by an unusual volatilisation process, or by entrainment (for example, of Al_2O_3, either present in the waste, or caused by the oxidation of small pieces of metallic aluminium in the combustion chamber). While small scale furnace studies suggested that aluminium may be volatilised in some limited circumstances, none of the thermodynamic calculations predicted volatilisation of aluminium, with the metal being split between pure solids and slag. In summary, the majority of aluminium is to be found in bottom ash, and no major volatilisation pathways have been found, with limited transfer to the fly ash being mainly by entrainment

6.1.2 Antimony

Due to sensitivity problems with antimony, this metal was not detected reliably in bottom ash samples, and the detection in cleaned flue gas suffered from problems of

interference, again related to poor detection sensitivity. However, antimony was detected in fly ash and APC residue, and in the un-cleaned gases from MSW incineration, at about 0.2 mg m^{-3}, a high level considering the low natural abundance of this element. Therefore, our experimental data indicates that volatilisation of antimony is almost complete. The relative concentration of antimony in flue gas, compared with that in bulk fly ash suggests that the majority of transport is evaporative, rather than by entrainment.

Thermodynamic predictions for antimony suggest that complete volatilisation will only occur at higher combustion temperatures, with slag phases and pure solids being important at lower temperatures. When enhanced dissolution of Sb in the slag was permitted, antimony volatilisation was inhibited. Chloride species are not significantly involved in volatilisation, so altering the alkali or chlorine content of the waste has little effect on antimony distribution during incineration. None of the other variables studied had a significant effect on antimony behaviour either. Thus it is seen that although slag formation may inhibit antimony volatilisation (seen for the bulk waste with enhanced slag formation model, and CRT glass), this appears to happen little in practice, hence the failure to detect antimony in bottom ash. In the absence of slag formation, antimony is almost exclusively transferred to the flue gas, though it is removed before atmospheric discharge of the gas.

6.1.3 Arsenic

Experimental data for arsenic was extremely limited. It was detected in incinerator solid residues at the low-ppm level, but sensitivity issues meant that measurements were unreliable, as they were near the detection limit. Similarly, although As was monitored in cleaned flue gas, no specific events were noted in the emission profile. Unfortunately, arsenic was not measured in the un-cleaned flue gas.

Thermodynamic calculations predict arsenic to be primarily found in an oxide-slag melt, with little or no volatilisation. In the absence of reliable experimental data, this is presumed to be the case, though further information on this element would be most helpful.

6.1.4 Cadmium

Cadmium was found at a concentration of about 100-150ppm in fly ash, and around 50ppm in bottom ash. Although not found in significant concentration in cleaned flue gas (partly due to instrument sensitivity and matrix interference issues), significant spikes of cadmium were observed in the cadmium profile in un-cleaned flue gas, with near-zero concentrations being recorded apart from the spikes. The spikes were up to 0.2mg m^{-3}, a high concentration for such a toxic metal, and were of a few minutes duration. The appearance of such spikes was apparently random, and un-correlated to incinerator operating conditions, and the presence of cadmium was confirmed on multiple emission lines by examining the spectral scans recorded by the instrument. It is thought that such spikes would be caused by specific discrete sources of cadmium in the waste, such as a nickel-cadmium battery.

Given that the measured concentration of cadmium in the flue gas and the total gas volume flow rate through the incinerator had been measured, this information could be used to calculate the total mass of the metal present in the flue gas (as vapour or small particulates) to cause the size of peak observed (21):

$$M_m = \sum_{T=0}^{T=1} C_m F_{NTP} \quad (21)$$

Where M is the total mass of metal accounted for (g)
T=0 is the start of the calculation period (s)
T=1 is the end of the calculation period (s)
C_m is the measured concentration of the analyte [in this case cadmium] at NTP (mg m^{-3})
and F is the flow of gas for this period at NTP ($m^3 s^{-1}$)

An individual peak (as seen in Figure 99 [Page 195]) was calculated to correspond to up to 1g of metal. For a 4 hour monitoring period, the total mass of cadmium accounted for in the flue gas was 4.47g, with 2.63g of this being accounted for during the 6 clearest peaks, over a period of 26 minutes. Thus 59% of the cadmium in the flue gas is accounted for in 11% of the time, indicating that the temporal variation in concentration is highly significant.

It is believed that the most significant source of cadmium in municipal waste will be nickel-cadmium batteries. A typical "AA" size Ni-Cd cell weighs about 25g, and is composed of up to 50% Cd by mass. Therefore, one of the smaller Ni-Cd cells available would contain about 12g of Cd metal. Assuming the quantification of the measurements made is reasonable, this would suggest that only a relatively small proportion of the Cd is volatilised.

General thermodynamic predictions (without enhanced slag dissolution of Cd) suggest that cadmium is completely volatilised above 850°C. However, if CdO is allowed to dissolve in the slag, volatilisation is significantly reduced, except at the highest temperatures. Studies into the effect of changing waste composition do not show any dependence on waste matrix, as volatilisation is always dominant at the temperature studied, without the use of enhanced slag formation models. Nevertheless, volatilisation of cadmium is significantly retarded when specifically considering the equilibrium around a nickel-cadmium battery (just 4% at 1050°C), and at higher oxygen levels, due to the formation of less volatile CdO (compared with Cd, the main volatile species). Given this information, it seems reasonable once more to attribute cadmium peaks in the emissions profile to discrete sources of Cd in the waste, such as Ni-Cd batteries. The near-zero concentration of cadmium apart from these peaks suggests that slag formation may help to minimise Cd volatilisation from more homogeneous Cd sources.

Given that cadmium is found both in bottom ash and fly ash, the data obtained suggests that oxidation of cadmium may be significant, such that although cadmium is found as significant spikes in the un-cleaned flue gas, sufficient material is not volatilised such that cadmium is still found in a measurable (and probably environmentally significant) concentration in the bottom ash. Given the high toxicity of cadmium, the presence of cadmium as spikes of high concentration in flue gas, and presumably in APC residue must be of concern, as occasional high concentration areas are far more likely to be harmful than a lower, uniform concentration in the residue. The most effective way of addressing this problem would be to remove the sources of cadmium from the municipal waste stream prior to incineration: quite simply, if point sources of cadmium in the waste are removed, the problem of cadmium in incinerator

residues is effectively eliminated, and better facilities for alternative disposal of this extremely toxic metal would facilitate this.

6.1.5 Calcium

High concentrations (~12%) of calcium are found both in bottom ash and APC residue (which has had lime added to it). Calcium was observed in the cleaned flue gas at a concentration of up to about 0.05 mgm^{-3}, not a concentration which causes concern, as the element is non-toxic, but a level which indicates that measurements were successful. More calcium was seen in the un-clean gas (up to about 0.2 mgm^{-3}, excluding spikes). Occasional spikes were observed in the profile, which were not linked directly to process events, but the general periodic fluctuation in the signal corresponded with the changing oxygen level in the furnace. Given that increased oxygen level will correspond in part to increasing flow of air through the furnace, it is thought that the link is due to increased entrainment at higher flows. Unlike aluminium, it would appear that significant amounts of calcium are entrained at particle sizes which can be analysed by the CEML. The source of the larger spikes (up to about 0.6 mgm^{-3}) is unknown, and may be due to entrainment or volatilisation.

Thermodynamic predictions for calcium are that the metal is non volatile in normal combustion, being partitioned between the pure solid and slag phases, irrespective of the variations in input composition. However, the equilibrium calculation for a PVC window profile predicted the formation of $CaCl_2$ in significant quantity, leading to volatilisation of 3.5% of the Ca at 1050°C, and 100% at 1300°C. Thus a possible explanation is offered for how occasional peaks in the un-cleaned flue gas profile may arise by volatilisation, due to local equilibrium around specific items of waste. However, this has not been proven experimentally, and the possibility of an entrainment "event" cannot be excluded. Nevertheless, the results are extremely interesting, as they demonstrate a possible volatilisation route for a metal which has previously been considered completely non-volatile during waste combustion.

6.1.6 Chromium

Chromium is found at a concentration of about 100-200 ppm in both bottom ash and APC residue. The emission line used for continuous monitoring had excellent sensitivity, and chromium was not observed at significant concentration in either emitted or un-cleaned flue gas, with no spikes being seen in the profile. It is assumed therefore that any chromium found in the APC residue arrives there by entrainment.

Thermodynamic calculations do not predict chromium to be significantly volatile. Although a small amount of CrO_2 is predicted to be volatilised at 1300°C, none of the other variables have an effect on chromium partitioning, and chromium was not an element considered in any of the specific item equilibriums.

Thus chromium is confirmed to be essentially non-volatile, and probably does not present significant concern in the bottom ash, where it is present as an oxide, either as a pure species or dissolved in the slag.

6.1.7 Cobalt

Cobalt is found at about 50ppm in both bottom ash and APC residue. Despite high detection sensitivity, cobalt is not found in significant quantity in cleaned or un-cleaned flue gas, and there are no notable features on the profile, except for a tendency to follow oxygen concentration in the un-cleaned gas.

Thermodynamics predict that cobalt could be very slightly volatile at temperatures over 950°C, and high chlorine concentrations could slightly increase volatility, although high oxygen concentrations would inhibit volatilisation. Nevertheless, the majority of cobalt was found as pure solid. Given that intense combustion is likely to cause simultaneous high temperature and low oxygen, this aspect of the prediction is probably not particularly important. Various chlorides of cobalt are implied in transportation, and so consequently high chlorine or low alkali concentration would favour volatilisation, and visa-versa. However, the majority of cobalt is found as pure solid or in the slag, depending on the slag solution model used. Cobalt was not found to be volatile in nickel-cadmium batteries, where it is present as an impurity. However, there was no experimental support for the predicted volatility, and it appears from experiment that cobalt is in fact entirely non-volatile. Enhanced slag formation models for Co in general MSW incineration suggest that slag formation may significantly reduce volatilisation, and the experimental results suggest that this is indeed the case.

6.1.8 Copper

Copper is found at about 3000ppm in bottom ash, and up to 1000 ppm in APC residue. Thus the majority of copper is retained in bottom ash. However, both copper (I) and copper (II) chloride were found to be volatile in a test furnace, and although copper was not found in significant concentration in the cleaned flue gas, it was found in significant concentration (~0.1 mgm^{-3}) in the un-cleaned gas. Significant fluctuation was seen in the concentration profile with time, which corresponded somewhat, but not exclusively to oxygen concentration (and hence entrainment).

Possibly the most interesting observation about the copper emission profile is the association with other metals. There are some peaks in the copper profile which are in common with other metals, both volatile and non-volatile, including sodium, supporting the fact that copper transport is linked to bulk incinerator properties. However, during comparison of the copper profile with other metals, it was found that the closest association for some parts of the profile was with lead, although this does not correlate well with sodium, indicating the dependence of copper on two other metals, not an interdependence of these two metals. The exact reasons for such an association with lead are not clear, but both metals are primarily predicted to volatilise through chloride formation, with high chlorine or low alkali favouring volatilisation. Although no "specific items" containing both elements were considered, both electronic items and plumbing waste tend to contain both, and a chlorine-limited equilibrium could possibly lead to the observed results.

6.1.9 Iron

Iron is present at about 6000-7000 ppm in APC residue, and about 5-6% in bottom ash, meaning that the majority of the iron is not volatilised during incineration. However, as incinerator components are made of iron containing materials, outliers are sometimes seen in APC and fly ash values, due to contamination with incinerator oxidised construction material. Iron can be seen in the emitted flue gas, but is not found at high concentration. In contrast, it is found at up to 0.1 mgm^{-3} in un-cleaned gas, relatively high for a metal which is generally considered non-volatile. There is significant temporal variation in the concentration profile, with several spikes, which are not readily correlated to incinerator operating conditions. These events could be linked to boiler corrosion events, which remove ferrous material from which the

incineration plant is constructed. Other metal salts, such as V2O5, ZnCl2 and PbCl2 have been linked to such corrosion phenomena (Daniel et al., 1988, Bryers, 1968, Bryers, 1996).

Thermodynamic predictions do not suggest volatility of iron in general MSW incineration, irrespective of changes in operating conditions or waste composition. Iron does not participate significantly in slag formation, and is present mainly as pure solids. Calculation of the equilibrium around a zinc-carbon battery, however, does suggest volatilisation of a small amount (0.2%) of the iron (in the casing) at 1300°C, as iron (II) and (III) chloride.

It is not certain whether the observed spikes in concentration in un-cleaned flue gas are caused by the volatilisation or entrainment of iron. However, unique predictions of equilibrium around specific items in the waste stream suggest a possible volatilisation route, which would not normally be considered.

6.1.10 Lead

Lead is found at about 1000ppm in bottom ash, and 1000-2000ppm in fly ash. Experiments with a laboratory furnace showed lead to be non-volatile, while lead(II) chloride was easily volatilised (although evidence from lead smelters indicates that the metal itself can be volatile). Further furnace studies showed that lead could be volatilised by other metal chlorides, such as zinc or tin, showing that lead chloride formation was highly favoured. Fortunately, lead is not seen in significant quantity in cleaned flue gas, it not being apparent whether observed variation is due to signal variation or background noise. However, lead concentrations in the un-cleaned gas are extremely high (up to 1.5 mgm^{-3}), and exhibit significant temporal variation, which is not directly linked to plant operating conditions.

Compared with sodium, for which transfer to the gas stream is linked strongly to bulk plant conditions, lead exhibits greater overall variation in flue gas concentration, with time, on a scale of several minutes to hours. For sodium, the average emissions over any half-hour period are broadly similar, whereas for lead, some are noticeably higher than others

Using sodium and potassium as "reference" metals, whose concentration in the un-cleaned flue gas is attributed almost entirely to bulk plant conditions, the long-term variations in lead are interesting. The short-term variations correlate well with sodium and potassium plots, indicating dependence on bulk plant conditions. However, the longer-term temporal variations in lead, with general regions of "higher" or "lower" relative lead concentration, typically lasting around 30 minutes, must be presumed to be due to variation in lead in the feed waste, with wastes with both relatively high and relatively low lead content being fed during the monitoring period. As for most other toxic heavy metals, the majority of the lead in MSW is found a relatively small proportion of the waste, and the implication of the variation observed is that better separation of lead-containing wastes could significantly reduce the concentration of lead in incinerator residues.

Thermodynamic predictions are that lead (as lead II chloride and PbO) is highly volatile in typical municipal waste, although strangely, volatility is higher at low temperatures, as slag formation at higher temperatures inhibits volatilisation. The equilibrium is affected by chlorine and alkali concentration, and a little by oxygen and

water concentration, though not by sulphur concentration. Although lead is completely volatilised from isolated PVC combustion (if it contains lead), slag formation inhibits lead volatilisation from CRT glass, so although volatilisation still occurs, some remains in slag. Similarly, the volatilisation of lead from isolated solder is reduced at low temperatures, although in this case slag formation is not predicted.

Thus it is seen that although lead is largely volatile, it is not exclusively transferred to the flue gas and APC residue. Again, thermodynamic predictions of local equilibria around specific items in the waste offer explanations as to why this may be.

6.1.11 Magnesium

Magnesium is found in similar concentrations in bottom ash and APC residue, at around 10000 ppm. It is not seen in significant quantity in un-cleaned or emitted flue gas, implying it is mainly transported by entrainment.

This supposition is supported by the thermodynamic calculations, which do not predict the volatilisation of magnesium in any circumstances, although it should be noted that this element did not feature in any of the "local equilibrium" calculations.

6.1.12 Manganese

Manganese is found at concentrations of 600-700 ppm in bottom ash, and 500-600 in APC residue. It was not found in significant concentration in cleaned or un-cleaned flue gas, and no significant temporal variations were observed, hence it is assumed that any transfer to the flue gas is by entrainment.

Thermodynamic equilibriums show that manganese is essentially non-volatile, though a little volatilisation (<1%) of $MnCl_2$ is predicted, with a dependence on chlorine and alkali concentration. Manganese remained mainly non-volatile in "specific item" equilibrium calculations, although the amount of volatilisation increased slightly in the case of a zinc-carbon battery. However, the main finding for this metal is that manganese is not significantly volatile.

6.1.13 Mercury

Thermodynamic calculations always predict 100% volatilisation for mercury, and as it was not detected in bottom ash, this prediction has not been questioned. However, due to the analytical procedures involved (the heated extraction process), neither was mercury found in the solid residues.

However, mercury was found in significant concentration in un-cleaned flue gas, with the emission pattern resembling that of cadmium. Once more, it is thought that specific items in the waste would lead to these emissions, which were confirmed by examination of the spectral scans of multiple mercury emission lines.

For one part of the measurement period, mercury levels in the emitted gas were found to be high, but this spike was not of significant duration, and is believed to be a "one-off" event.

However, a major spike (8 mgm^{-3}) of mercury was observed in the un-cleaned flue gas. This spike was far higher than anticipated, and although it was unambiguously identified as being mercury, the question arose as to the source of such a large mercury source. The result of calculation of the amount of mercury required in the waste feed

to produce that emission event (as for cadmium in section 6.1.4) was that about 90g of mercury must have entered the furnace to cause the emissions, which lasted about and hour and a half.

Obviously there must have been a significant point source of mercury in the waste feed, either several thermometers, a mercury barometer, or similar. Such an item in the feed is possible, but is unlikely to be frequent, and it is just coincidence that such an event happened during the monitoring period. Although caution should be exercised when interpreting the quantification of such large signals (over the highest calibration standard measured), particularly for an element with such a notorious "memory effect" in analytical systems, it is quite certain that an unusual event in the mercury concentration profile was observed by continuous monitoring, and is attributed to a specific source of the metal in the feed waste. Once more, the need for improved management of such toxic waste materials is highlighted. Better public information and more readily available alternatives to putting hazardous items in with general waste could have a significant impact on such undesirable events.

6.1.14 Nickel

Nickel is found at a concentration of about 50ppm in both bottom ash and APC residue, but is not measured in significant concentration in cleaned or un-cleaned flue gas, despite being monitored on a highly sensitive emission line. Thus it is seen that nickel is non-volatile, with any transfer to the flue gas being by entrainment.

Equilibrium calculations predict that nickel will be slightly volatile (~1%), with a dependence on chlorine concentration, and also alkali concentration as a result. However, there is no prediction of volatility for nickel in a nickel-cadmium battery. Thus it is seen how local conditions may lower the volatility to meet observations, as well as raising it, as has been seen for other metals

6.1.15 Potassium

Potassium is a volatile metal, being found at a concentration of about 2.5% in APC residue, and about 0.4% in bottom ash. Potassium is found in high concentration in un-cleaned flue gas (5-15 mgm^{-3}), and significant temporal variation is observed. However, it is effectively removed from the flue gas during clean-up, leaving a small though detectable concentration.

Potassium concentrations in the un-cleaned flue gas are closely correlated to sodium concentrations, and it is thought that both are linked to plant operating conditions (temperature and oxygen). A full explanation for such close correlation between the concentrations of the two metals has yet to be found, though the general properties of these two group 1 metals tend to be very similar, although it should be noted that the ratio of Na:K in the flue gas is not simply a function of their relative concentrations in the waste, but also of their thermodynamic properties.

Potassium is predicted to be volatilised between 0.3 and 76% in typical municipal waste, depending on the temperature. Changing alkali or chlorine content can alter that figure by about 10%, though the effect of other variables examined is smaller, though noticeable. Equilibrium around an alkali or nickel-cadmium battery exhibits greater volatilisation of potassium, while slag formation in CRT glass reduces volatilisation almost to zero.

Thus it is seen that volatilisation of potassium is highly dependent on combustion conditions, explaining the variability seen in the concentration of the metal in the un-cleaned gas.

6.1.16 Sodium

Sodium is found at a concentration of about 1-3% in APC residue, and less than 0.5% in bottom ash. Given that about 10 times more bottom ash is produced than APC residue, this would correspond to about 20% volatilisation of Na. Concentrations in the un-cleaned gas vary significantly over time, and are thought to link to bulk operation conditions, as explained above for potassium. It is also assumed that changing waste feed will affect sodium content in the waste, and hence the concentration in the flue gas.

Although sodium is found in significant concentration in un-cleaned flue gas (6-10 mg m^{-3}), it is effectively removed from the cleaned gas, leaving a concentration at or about the limit of detection.

Thermodynamic predictions are that up to about 10% of Na is volatilised, with temperature and chlorine having a significant effect. However, sodium is an effective slag-forming element, and this reduces volatility, as seen for the equilibrium for CRT glass. In general, the results of thermodynamic prediction are in good agreement with the experimental data, when taking into account the fact that some entrainment will also occur.

6.1.17 Thallium

Thallium was not detected, either in solid residues, or in flue gas, mainly due to the poor sensitivity of this element in ICP-OES analysis. However, the lines were monitored, and had there been significant thallium peaks, no doubt they would have been detected. Thallium was not included in the thermodynamic predictions, due to the scarcity of data for this element, and so little more has been learnt about its behaviour. However, the available indications are that it is not present in high concentration in the incinerator at any point.

6.1.18 Tin

Tin is found at concentrations of about 500ppm in APC residue, and up to 1000ppm in bottom ash, implying that the majority of tin is not volatilised during MSW incineration. Although tin is not found in significant concentration in clean flue gas, it is found at up to 0.2 mgm^{-3} in un-cleaned gas, with significant temporal variation, largely associated with plant oxygen level (and hence transport by entrainment).

Thermodynamic calculations do not predict tin to be volatile, except at the highest combustion temperatures (1300°C), with volatility being further reduced when the enhanced slag solution model for general MSW incineration was used. At the temperatures considered, altering the waste composition did not affect the equilibrium position, and tin remained non volatile. Neither was tin significantly volatilised in the equilibrium around lead solder. It is therefore assumed that tin volatilisation is caused by hot-spots on the burning bed, hence correlation with peaks for other volatile metals in the un-cleaned gas. The link to plant oxygen also suggests that entrainment is important for this metal. However, laboratory furnace experiments that tin could be volatilised in specific conditions in the presence of chlorine, with the reaction being inhibited by sulphur. This phenomenon was not supported by the thermodynamic

calculations made, but again serves to illustrate how local conditions may affect the overall volatilisation of a metal.

6.1.19 Vanadium

Vanadium is found at a concentration of about 200ppm both in bottom ash and APC residue, meaning that the majority of this element is not volatilised. It was not found in significant concentration in either the cleaned or un-cleaned flue gas, though measurement sensitivity was excellent. Thus the non-volatility of vanadium is supported by all measurements made. Vanadium was not included in the thermodynamic predictions, due to data availability, and the understanding that vanadium was generally "non-volatile" in any case. The work here confirms this supposition.

6.1.20 Zinc

Zinc is found at a concentration of about 0.7% in bottom ash, and 0.2% in APC residue. Although the metal is significantly volatilised, the majority of it is still found in bottom ash. Although measurements of zinc in cleaned flue gas were limited, available measurements indicate that, along with all other metals (with the possible exception of mercury), zinc is effectively removed from the cleaned gas. However, zinc is found in significant quantity in the un-cleaned gas (up to 0.2 mgm^{-3}), and there is significant temporal variation, linked with plant oxygen, and also correlating to the concentration of sodium and other metals. Thus it appears that both entrainment, and bulk incinerator operating conditions (such as temperature) may affect metal concentration in the un-cleaned gas.

Thermodynamic calculations predict that about 5-10% of zinc is volatilised under normal waste combustion conditions, but this proportion increases substantially with increasing chlorine or decreasing alkali, reflecting the importance of chlorine in volatilisation. The temperature dependence is less significant, as are other variables examined for the waste feed, although they do have some effect. Equilibrium predictions for specific items in the waste stream show that zinc volatility is suppressed in alkali battery combustion, where chlorine is used in KCl formation, but is enhanced in zinc carbon battery combustion, where large amounts of $ZnCl_2$ form. Such predictions are supported by small scale furnace reactions, where it is seen that $NiCl_2$, $PbCl_2$, and $CuCl_2$ all enhance zinc volatility.

Thus the thermodynamic predictions and experimental data are in good qualitative agreement, and once more it is seen how important local equilibrium may be in determining metal partitioning.

6.2 Summary

Numerous experiments, using both conventional techniques, and state-of-the-art continuous emissions monitoring, have been used to increase the available information on the behaviour of metals during waste incineration. It has been shown that significant temporal variation can be seen for some metals, which can be linked both to changing waste feed, and to changing incinerator conditions, both local, and for the system as a whole. Sophisticated thermodynamic equilibrium predictions have shown that changing plant conditions can have a significant effect on metal volatilisation, and predictions of local equilibrium around specific items in the waste have shown how inhomogeneity in the waste feed could lead to spikes in metal volatilisation. However,

it has been shown that flue gas clean-up is consistently effective, with no significant concentration of any metal being detectable for more than a few minutes in the emitted flue gas, with concentrations in the main being temporally stable, and below limits of detection, essentially corresponding to a measurement of zero concentration.

Although new and interesting measurements have been obtained, they are nevertheless in good agreement with what is already known about incineration of waste. However, temporally resolved measurements have shown just how much variation occurs on a minute-by-minute basis. Careful consideration of equilibrium both of the whole system, and locally around specific items on the burning bed have demonstrated why this may be so, and so new insights have been gained into how metals behave during incineration.

Chapter Seven:

Conclusions and Recommendations for Future Work

7.1 Conclusions

This thesis has described the successful systematic investigation into the behaviour of metals in municipal waste incineration. Unique information has been obtained on temporal changes in metal concentrations in incinerator flue gas, using an analytical system specially developed for that purpose. Experimental evidence has been compared with state-of-the-art thermodynamic predictions, which have largely accounted qualitatively for the observed behaviours. The following conclusions can be drawn from this research:

- Continuous Emissions Monitoring Laboratory Development:
  - A new mobile analytical system, based on conventional ICP-OES analysis has been developed to enable the study of metal concentrations in a difficult and changeable flue gas matrix.
  - The capability of the instrument has been demonstrated through laboratory experiments, and in an industrial environment, using the flue gases from a municipal waste incinerator, both before and after gas clean-up.
  - The CEML has been shown to work accurately, to a high degree of sensitivity, for numerous elements, despite the changing sample matrix.
  - The system was shown to be robust and adaptable. Not only has it been used for the analysis of conventional liquid samples, but it has also been used in an industrial setting to monitor both highly contaminated un-cleaned flue gas, where less robust systems would have struggled to make measurements at all, and to monitor cleaned gases, where a high degree of sensitivity was required.

- Continuous monitoring of metal concentrations in flue gas from municipal solid waste incineration:
  - The CEML has been used to make unique measurements of the concentration of various metals in the flue gas from a municipal waste incinerator, both before and after gas clean-up. Success in sampling a heavily dust-laden stream represents an important step forward in diagnostic technology.
  - Measurements of emitted flue gas have demonstrated the efficacy of the flue gas clean-up system in removing metal pollutant spikes. The emitted flue gas is essentially free from almost all metallic contamination, with the exception of occasional small amounts mercury, which nevertheless falls well within legislative limits overall.
  - Measurements of un-cleaned flue gas have proven the existence of metal pollutant spikes, which can be related to changing combustion conditions, and changing waste input. Therefore, changing waste disposal practice for certain key items could significantly reduce the problem caused by heavy metals during MSW incineration.

- Thermodynamic modelling of metal volatilisation and condensation during waste combustion:
    - A detailed calculation has been made using one of the most sophisticated packages available, in order to predict the products from combustion of all the typical constituents of municipal solid waste in equilibrium with one another.
    - A series of calculations produced a sensitivity study to assess which variables in waste feed composition and combustion conditions had the largest effect on the thermodynamic equilibrium. Combustion temperature and chlorine and alkali content of the waste were found to be most significant. It was seen that the nature of the slag formation model used had a critical effect on the distribution of some heavy metals, although data availability meant that the choice of model was not straightforward, and the assumptions required to obtain dissolution were significant.
    - Unique calculations have considered the equilibrium around specific metal-containing items of waste in a combustion gas matrix. These have shown how local non-equilibrium conditions, caused by waste inhomogeneity may have a significant effect on metal partitioning, either enhancing or suppressing metal volatility.

Data from continuous emissions monitoring of an operational incinerator, laboratory combustion tests, thermodynamic modelling, and conventional chemical analysis were combined to provide new insights into the behaviour of metals during waste combustion. Unique measurements of metal concentration have been made in the harshest of environments; the particulate-laden, changing composition matrix of flue gas from a commercial municipal waste incinerator. The study as a whole has provided new information, leading to an overview of the metal concentrations in incinerator flue gas and solid incinerator residues, how they are determined, and how they vary over time. This represents a significant advance in our understanding of such complex combustion systems.

The results show quite clearly that significant spikes of some toxic heavy metals, such as lead, cadmium, and mercury are caused by the presence of relatively small specific items in the waste, for example nickel-cadmium and lead-acid batteries. Better public education and improved availability of alternative disposal routes for such items could have a major effect in reducing the presence of these metals in MSW incineration, and so reduce the environmental burden caused by the incineration process substantially, at relatively low cost, and without significant technological requirements. Nevertheless, measurements have provided reassurance that metal emissions to atmosphere remain well within safe regulatory limits. Thus the work is both of benefit to the combustion science and technology community, and to the wider public, demonstrating not only that the combustion process is already well controlled and operating safely, but also how simple changes to waste handling procedures could bring environmental benefits for everyone.

7.2 Recommendations for Future Work

The work completed has demonstrated the viability of continuous measurement of metal concentrations in gas streams from industrial processes, and shown how these can give new and valuable information about such systems. The use of thermodynamic modelling techniques to examine equilibrium in waste combustion, including variable sensitivity studies, has shown how metals typically behave during incineration. Consideration of local equilibrium around specific items has shown how unusual partitioning behaviour may arise from local equilibrium conditions, due to waste inhomogeneity. However, as these are some of the first investigations of their kind in such demanding situations, there is considerable potential to improve the quality and extent of the information obtained, and to extend the applications of the techniques to other systems. The following points have been identified which would benefit from further work, following this initial investigation:

- Development of the CEML:
  - Refine the primary sampling system for highly contaminated gases, to reduce drift caused by deposition, and decrease instrument down-time.
  - Complete full verification of the quantification of results, by comparison with the EPA standard method 29.
  - Extend the elemental capabilities of the detection and calibration system, to include detection of anions such as sulphur, and halogens, as well as metals/metalloids, whose detection has proved difficult to date.
  - Improve the automation of the analytical procedure in order to reduce operator dependence, and improve viability as a long-term un-supervised emissions monitor.
  - Improve the detection of larger particles which must currently be excluded from analysis. This may possibly be achieved by using a laser ablation system to break up the large particles, in a preliminary stage before ICP-OES analysis.

- Thermodynamic modelling:
  - The ability to obtain good thermodynamic results is limited by data availability, particularly for complex slag solution melts. Extending multi-element slag models, particularly for chlorine, carbonate, and other melt-forming species would improve model accuracy, and would thus be of great benefit.
  - Results obtained using new approaches of "local equilibrium" to consider the effects of inhomogeneity in a system have proved most successful on a qualitative level. Further quantitative validation of such models would be of value, as would extension to further "specific items", and possibly to other inhomogeneous systems where thermodynamic equilibrium calculations would be of use.

- Investigation of the behaviour of metals in municipal waste incineration:
  - Combine the use of the CEML for stack gas monitoring with a detailed study of the input to an incinerator, so that emissions can be better linked to waste feed characteristics.
  - Use the CEML at one of the large scale research-equipped municipal waste incinerators, where the information available on the conditions in the furnace are more detailed, in order to better correlate plant conditions to metal emissions.

- Utilisation of the techniques developed:
    - Further, longer term monitoring of metal release during waste incineration would be of value, to see longer-term trends and possible seasonal variation.
    - The CEML should be fully capable of making measurements of metals in other industrial processes which release metals (e.g. electricity generation by coal combustion, metal extraction and processing, bio-fuel combustion, hazardous waste incineration). Use of the laboratory to study such processes could lead to new information on metal emission, which may lead to strategies to help to reduce emissions.
    - The CEML could be used with a laboratory burner, to validate the predictions for equilibrium around specific items in the municipal waste stream.

- Extension and coupling to new techniques:
    - There is substantial potential to use the CEML in conjunction with other analytical techniques, to provide even more detailed and valuable information on combustion by-products:
    - Use of the CEML with sophisticated particle size-separating instrumentation (Andersen samplers), along with detailed study of selected particulates and deposition on their surfaces by electron microscopy and x-ray analysis, to gain characterised size distribution data. This should allow differentiation between particles arising from entrainment and from evaporation/condensation mechanisms.
    - Use of the CEML and other technologies for the identification and characterisation of the nanometre and sub-nanometre particles recently identified in biomass combustion gases.

Thus it is seen that although the value of the study into the behaviour of metals in municipal waste incineration has already been clearly demonstrated, there is still the potential for considerable further study, both of metal pollutants in municipal waste incineration, and of other metal-releasing processes. Indeed, the list of possible further work is not exhaustive, and possible future applications extend well beyond those which it is possible to detail here, due to the highly successful nature of the techniques developed, and applied to this specific situation.

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Appendix 1: Publications and Conference Presentations

Refereed Journal Publications

Poole, D.J., Sharifi, V.N., Swithenbank, J., Ardelt, D., ***Identification of metal concentration fluctuations in waste-to-energy plant flue gases – a novel application for ICP-OES***, Journal of Analytical Atomic Spectrometry 2005. **20:** 932-938

Poole, D.J., Sharifi, V.N., Swithenbank, J., Argent, B.B., Ardelt, D., ***Identification of Metal Pollutant Spikes in Municipal Solid Waste Incinerators by Continuous on-line Analysis*** (paper submitted to Waste Management May 2005).

Clarkson, P.J., **Poole, D.J.**, Sharifi, V.N., Swithenbank, J., Waarlo, H.-J., Ardelt, D., Falk, H., ***Continuous measurement of mercury in flue gas using ICP-OES.*** Journal of Analytical Atomic Spectrometry, 2004. **19(5):** p. 652-653.

Clarkson, P.J., **Poole, D.J.**, Ryu, C.K., Sharifi, V.N., Swithenbank, J., Waarlo, H.-J., Ardelt, D., Falk, H., ***Continuous Measurement of Metals in Flue Gas Using ICP-OES.*** Analytical and Bioanalytical Chemistry, 2003. **377(1):** p. 39-47.

National / International Conference Presentations

Poole, D.J., Sharifi, V.N., Swithenbank, J., Ardelt, D., ***Identification and Control of Metal Pollutant Spikes in Waste-to-Energy Plants - A Novel Application for ICP-OES***, European Winter Conference on Plasma Spectrochemistry, Budapest, Hungary, 30th January - 2nd February 2005.

Swithenbank, J., Sharifi, V.N, Yang, Y.B., Ryu, C.K., **Poole, D.**, Goddard, C., ***Tracking Micro-Pollutants from Cradle to Grave (plenary lecture)***, 9th International Conference on Combustion By-Products and their Health Effects, Tuscon, Arizona, 12th - 15th June 2005.

Clarkson, P.J., Gan, S., **Poole, D.**, Chang, B.F., Ryu, C., Nasserzadeh, V, Swithenbank, J., ***The Cutting-Edge of Micro-Pollutant Emission Measurements***, 4th International Symposium on Waste Treatment Technologies, Sheffield, UK, 29th June - 2nd July 2003.

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Clarkson, P.J., Ryu, C.K., **Poole, D.J.**, Sharifi, V.N., Swithenbank, J., ***Continuous Measurement of Metallic Species in Flue Gas using ICP-OES***, European Winter Conference on Plasma Spectrochemistry, Garmisch-Partenkirchen, Germany, 12th - 17th January 2003.

Clarkson, P.J., **Poole, D.J.**, Nasserzadeh, V., Swithenbank, J., ***Measurement of Metals in Flue Gas using a Continuous Emissions Monitoring laboratory***, 4th International Symposium on Waste Treatment Technologies, Sheffield, UK, 29th June - 2nd July 2003.

ARTICLE

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Identification of metal concentration fluctuations in waste-to-energy plant flue gases—a novel application for ICP-OES†

David J. Poole,*[a] Vida Nasserzadeh Sharifi,[a] Jim Swithenbank[a] and Dirk Ardelt[b]

[a] *University of Sheffield, Mappin Street, Sheffield, UK. E-mail: d.poole@sheffield.ac.uk; Fax: +44 (0) 114 222 7501*
[b] *SPECTRO Analytical Instruments GmbH & Co KG, Kleve, Germany*

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A mobile continuous emissions monitoring laboratory, based on ICP-OES technology, was used to study temporal variations in metal concentrations in the flue gas of a waste-to-energy plant. The concentrations of over 30 elements were monitored prior to flue gas clean-up. Despite harsh analytical conditions, with high particulate loading, variable gas matrix and high concentrations of numerous elements, semi-quantitative measurements were made. Realistic detection limits in the range 0.007–0.06 mg m^{-3} were achieved. For many volatile metals, significant variations (4–18 mg m^{-3} for Na, 0–0.18 mg m^{-3} for Cd) were observed, and were linked to properties of the metal in question, to incinerator operating conditions, and to variations in the waste feed charge. The concentrations of some metals were attributable to specific sources in the waste. It was concluded that better waste segregation could significantly reduce the concentration of toxic metals in the incinerator residues, and where concentration spikes were detected, accurate real-time metal concentration measurements had the potential to provide feedback to clean-up systems, thereby minimising the overall environmental effect.

Introduction

Households in the UK generate about 30 million tonnes of municipal solid waste every year, and the figure is still rising. The question of how to dispose of this material is a complex and emotive one, with none of the available options being ideal.[1] About 7% of this waste is incinerated, allowing energy to be recovered from the waste, and government guidelines mean that this proportion will increase in future.[2] Nevertheless, there is considerable public concern about the environmental and health effects of pollutants from thermal treatment of waste. Although a great deal is known about bulk pollutants such as CO_2, SO_2, NO_x and trace organic pollutants (*e.g.*, dioxins and furans), relatively little is known about volatile metals in the combustion system.[3] Emissions are measured periodically, by extractive testing, and so little is known about temporal variations in metal volatilisation. Nevertheless, thermodynamic predictions and other previous work suggests that they will be strongly affected by temperature, chemical environment in the bed, and metal content and distribution in the waste, and will therefore vary significantly over time.[4,5]

An individually constructed mobile laboratory, containing a specially configured ICP-OES system, has been used to obtain information on the concentration and variation of metallic pollutants in un-cleaned flue gas from a waste combustor. This unique continuous emissions monitoring laboratory (CEML), designed around a commercially available ICP-OES system (SPECTRO CIROS CCD, SPECTRO Analytical Instruments, Kleve, Germany), and equipped with a 40 m heated sampling line, was used to simultaneously monitor the concentrations of over 30 elements including the volatile metals Cd, K, Na, Pb, Sn and Zn, with a time resolution of one minute.

Experimental Continuous Emissions Monitoring (CEM) techniques for gas streams began appearing in the literature in the mid-1990s.[6–8] A variety of different analytical technologies have been employed, including laser induced plasma spectrometry,[9] dc spark spectrometry,[10] X-ray fluorescence spectrometry,[11] microwave induced plasma spectroscopy,[12] and inductively coupled plasma spectrometry.[13–15] A good review, and comparison of such technologies, is given by French, Haas, and Priebe.[16]

Broadly, the devices fall into two categories: those which are placed at or near the stack and therefore need to be relatively small, and those which opt for a larger analytical system, and therefore require more remote positioning and thus a more sophisticated sample transfer system. Smaller systems avoid some of the sampling problems caused by a longer sampling train, but often at the expense of a less sophisticated excitation or detection system. Irrespective of the specific design of the monitoring system, which are many and varied (the sampling train, plasma source, and detector), many of the problems encountered in continuous monitoring of flue gases are common to all the different techniques. These relate to maintaining reliability, sensitivity and accuracy in an unusual, variable and difficult matrix.[16,17]

Firstly, sample integrity is difficult to maintain, due to problems of achieving representative sampling, and particulate deposition on the sample collection system, which tends to lead to measurement drift and poor repeatability.[18] Subsequent sub-sampling (which may be required in order to obtain a sample volume appropriate for introduction to the detector) is a further source of sampling error, and although the principal researchers in the field (Trassy and Diemiaszonek, Meyer and Lee, Seltzer and Green) have experimented with different interface designs, none has been found to be without its problems.[17] Secondly, the composition of the bulk sample matrix (*e.g.*, concentration of combustion gases CO_2, H_2O) affects instrument sensitivity, leading to poor precision if the sample gas matrix varies with time. Effects are due both to spectral interferences (*e.g.*, from the CN radical which is formed when high CO_2 and N_2 concentrations are present in the plasma) and general plasma cooling due to high plasma

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loading, which also affects emission intensities.[8,19–21] Thirdly, difficulties exist over obtaining reliable calibrations for gas-phase metal concentrations, due to the lack of availability of suitable matrix-matched standards.[16,20]

Such difficulties mean that despite recent advances,[22–25] none of the monitoring systems have yet been found to meet the requirements for regulatory endorsement,[22,23,26] although it is understood that John Cooper hopes to receive approval soon for his X-ray fluorescence based system. This device is quite dissimilar from the other technologies, which all seek to measure particulate concentrations in the flue gas itself. Instead, continuous monitoring is achieved by passing flue gas through a carousel-mounted filter, and periodically conducting analysis of the collected material, giving a measurement about every 20 minutes.[27]

Following a period where there have been relatively few publications on continuous emissions monitoring systems for metals, recent work by Abanades *et al.* has given extremely valuable data on metal behaviour in relatively well controlled laboratory fluidised bed combustion systems. The detection system is developed from the design by Trassy and Diemiaszonek, and is essentially very similar to our own.[28]

The authors believe that they are the first to publish semi-quantitative data on rapid temporal variations in metal concentrations in flue gas from a commercial-scale waste incinerator, before any gas clean-up. Although promising work has been published by Timmermans *et al.* on measurements inside the furnace of a waste combustor, the results presented did not indicate metal concentrations, nor their temporal variations.[29]

Our analytical system is already well-proven, having previously been developed and used for flue gas analysis of the cleaned gas from the same plant,[30] and been quantitatively verified with laboratory furnace spiking experiments.[31] The highly contaminated matrix of un-cleaned gas presented significant analytical challenges, but the results are very encouraging, demonstrating the versatility and robustness of the ICP-OES as an analytical tool for process monitoring. The data obtained from this research is fundamental to understanding the temporal fluctuations in metal emissions from the incineration system, and represents a significant advance in the field of on-line emissions monitoring.

Experimental

The test site

Experiments were conducted at a commercial scale waste-to-energy plant. The plant had 2 lines, each with an average hourly throughput of 10 tonnes. The grate type was reverse reciprocating, and the furnace walls were water cooled, providing heat to the energy recovery system. Furnace temperature was measured using two thermocouples in the radiation shaft. Operational parameters were used to keep the temperature between 850 °C and 1100 °C, with further waste being added in response to falling temperature. The plant was operated with excess air, leading to an oxygen level in the combustion chamber between 6% and 14%, measured in the radiation shaft.

Flue gas treatment was by a hydrated lime and activated carbon dry scrubbing system. Fabric filters collected the fly ash and scrubber products, and were designed to remove particulate matter down to a minimum of 5 μm. The gas clean-up system was preceded by an economiser, which reduced the flue gas temperature to 130 °C at the bag filters. A standard 4″ BSP sampling port in a vertical section of ducting immediately prior to the scrubbing system was used in this work, with some comparison measurements being made at a sampling port immediately following the bag filter system. Mandatory testing conducted by the plant shows the clean-up system to be effective, meaning that the plant consistently meets legislative emission limits.

Analytical system

The mobile CEML used in this work has previously been described in detail.[30] Briefly, this system, built in collaboration with SPECTRO Analytical Instruments (Kleve, Germany), is used simultaneously to monitor the concentrations of multiple elements in flue gas from an industrial source, with a time resolution of one minute or less. It comprises an isokinetic sampling system, 40 m heated sampling line (to transport the sample continuously to the mobile laboratory), isokinetic sample interface and a SPECTRO CIROS CCD ICP-OES spectrometer. The spectrometer is capable of making simultaneous quantitative measurements of over 30 elements (wavelength range 125–770 nm), with one measurement being made per minute in this work. The entire system is built into a shipping container, easily transportable by road to allow on-site emissions monitoring. The laboratory forms an entirely self-contained unit, only requiring external sample, power and water supplies. Argon supply (CryoService, Worcester) is provided *via* an integral 230 L liquid supply tank, which allows about 5–6 days continuous operation. Thus, the CEML was used to make measurements of un-cleaned flue gas at the waste-to-energy plant described above, using the operating parameters given in Table 1.

The system was calibrated using multi-element aqueous standard solutions (Bernd Kraft GmbH, Duisburg, Germany), introduced into the gas stream as a dry aerosol using an ultrasonic nebuliser. Calibrations were conducted in a range of gas matrices, produced from reagent grade nitrogen, oxygen and carbon dioxide (BOC, Guildford, Surrey). These were introduced *via* mass-flow controllers, with gas compositions of 79% N_2 and 0–14% O_2, the remainder being CO_2. These data were correlated using multiple linear regression analysis in order to produce overall calibration curves for each monitored element line, linking line intensity both to analyte gas-phase concentration and matrix composition.

Sampling considerations

Achieving reliable analytical measurements in the un-cleaned flue gas was extremely challenging, despite a wealth of information already obtained on optimising the laboratory for clean flue-gas monitoring during previous on-site monitoring.[30] The un-cleaned gas provided a difficult analytical matrix, with very high particulate loading (~1 g m^{-3}), and high and variable concentrations of a number of metals, along with trace concentrations of others. The analytical system was designed for the sampling of small particulates and gases, with particle sizes not over 10 μm, so the sampling train used was designed to remove larger particulates (present in high concentration in the un-cleaned gas) with a small cyclone, as well as ensuring isokinetic sampling.[18] It was not our aim to sample large particulates, as volatile metals are enriched on the smallest particles (or are present as vapours within the combustion system).[32] Therefore, useful (semi-quantitative) results are only

Table 1 Main ICP operating conditions

Parameter	Value
Generator frequency/MHz	27.15
Power rf/kW	1.65
Plasma gas flow rate/l min^{-1}	20.0
Auxiliary gas flow rate/l min^{-1}	0.8
Aerosol carrier gas flow rate/l min^{-1}	0.5
Sample gas flow rate/l min^{-1}	0.125
Injector tube diameter/mm	1.8
Read time/s	44
Nebuliser desolvator temperature/°C	170
Nebuliser condenser temperature/°C	0

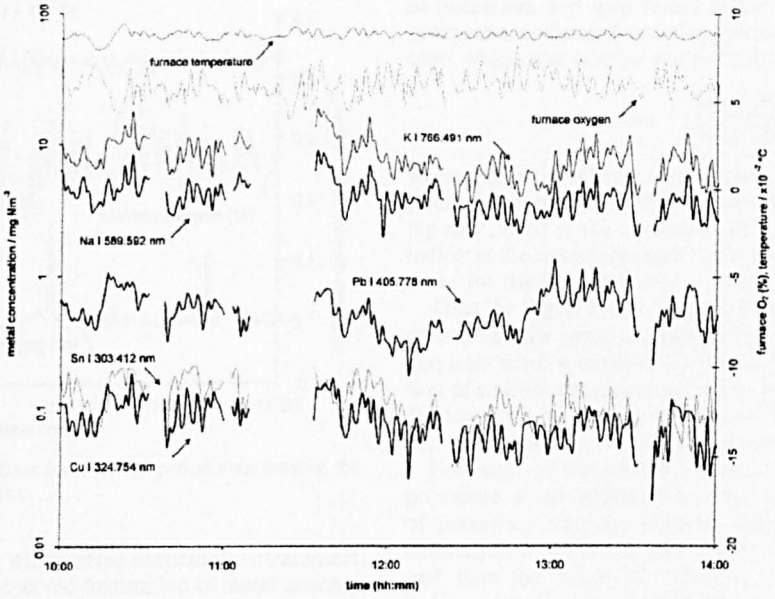

Fig. 1 Concentration–time profiles of various metals in un-cleaned incinerator flue gas for a 4 hour period.

available for the more volatile metals, with those being transported by entrainment of relatively large particles being generally under-estimated.

In addition to the data collected using the CEML, the measurements made by the plant operator during the monitoring time were collected. This included furnace temperature and oxygen (measured at the top of the radiation shaft), flue gas temperatures before and after the economiser, and temperature, oxygen content, moisture content and flow rate beyond the bag filters. These data were used to normalise the CEML results to standard reference conditions (273 K, 1 atmosphere, 11% oxygen, dry gas).[33]

Results and discussion

Emissions profiles

Numerous metal concentrations were measured continuously in the un-cleaned flue gas from the waste combustor. Illustrative concentration–time profiles (Figs. 1–5) show the variety of characteristic behaviours observed for different metals, and the links between different metals. In contrast to our earlier work, where metal concentrations could be measured uninterrupted for 24 hours or more, the nature of the sample matrix in this case meant that the longest continuous monitoring period was about 2 hours. At this interval, the sampling line was interrupted in order to empty the cyclone collector of particulate dust, and to check the probe assembly for blockage/deposition. This led to unavoidable short gaps in the emission profiles.

The concentrations of volatile metals in flue gas prior to cleanup were generally found to be extremely high, and significantly variable with time. Interpretation of the results was challenging, due to the large number of factors, which combine to produce the observed concentration profiles. Nevertheless, the analytical data shown below gives significant insight into how volatile metals behave under different incinerator conditions.

Sodium

Fig. 1 shows a typical concentration–time plot for sodium, potassium, lead, tin and copper. Also shown are the combustion chamber temperature and oxygen measurements made by the plant operator. Concentrations of sodium vary between about 2 and 8 mg m^{-3}, with emissions generally being low when furnace temperatures are low, and with periodic variations of about 2–3 min corresponding approximately to the changing oxygen concentration in the furnace. Oxygen concentration is thought to be an indicator for changing air flow

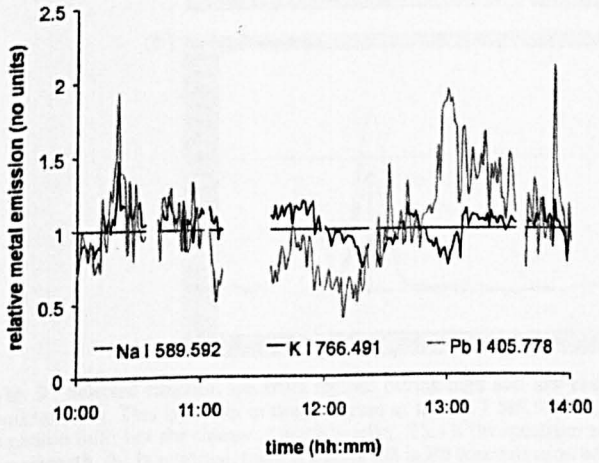

Fig. 2 Comparison of relative potassium and lead concentrations with respect to sodium for a 4 hour period.

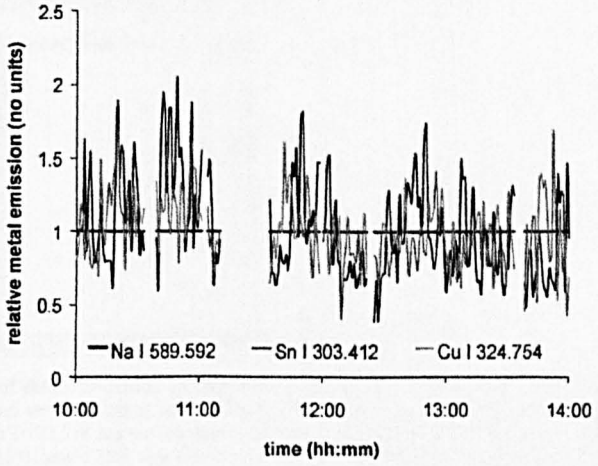

Fig. 3 Comparison of relative tin and copper concentrations with respect to sodium for a 4 hour period.

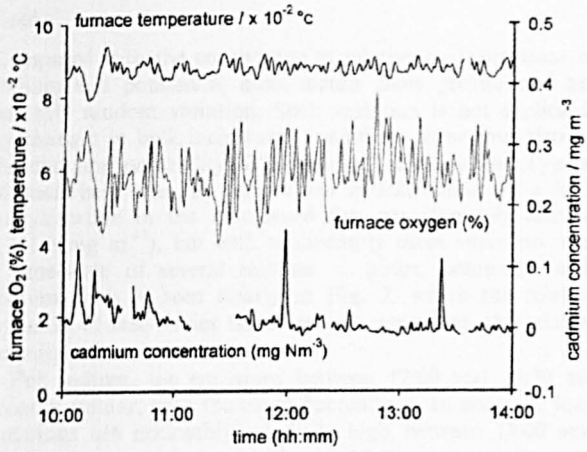

Fig. 4 Cadmium concentrations for a 4 hour period measured on the Cd II 226.502 nm emission line.

rates, as increased air flow will increase particulate entrainment in the gas phase, so the observed fluctuation in metal concentration is likely to be the result of a combination of changing thermodynamic environment (oxygen level) and physical parameters (entrainment). Although both of these factors affect metal transport, they do not fully explain the variation observed, which is also believed to be linked to changing waste characteristics and to the feed ram adding more waste to the furnace, resulting in disturbances on the bed, which lead to further entrainment. The high concentrations of sodium measured indicate that there is significant evaporation/condensation transport for this metal.

Potassium

Fig. 1 shows the concentration–time profile for potassium concentration, and Fig. 2 shows the relative concentrations of potassium and lead found in the un-cleaned flue gas at a given time, compared with the concentration of sodium at that time, which was worked out as follows:

$$C_{rel} = \frac{[M]_T/[Na]_T}{[M]_{av}/[M]_{av}} \quad (1)$$

where C_{rel} is the relative concentration of a specified metal at a given time (no units), $[M]$ is the concentration of that metal in mg m^{-3}, [Na] is the concentration of sodium in mg m^{-3}, T indicates the time-dependent value and av is the time averaged mean for the four hour period shown.

Thus the Fig. 2 shows the degree to which the concentration of one volatile metal is dependent on another (*i.e.*, sodium), and how much it varies independently. The relative concentration of sodium remains at one throughout, and the greater the deviation of the relative emission of another metal from one, the less related the two metal concentrations are.

For most of the monitoring time, the ratio of sodium to potassium is remarkably consistent, with the relative emission of potassium varying relatively little from one. The actual concentration of potassium is about twice that of sodium, and thus the range of potassium concentrations is about 4–18 mg m^{-3}. This correlation is attributed to the wide availability of both of these metals in the general waste charge (particularly in vegetable material, where the ratio of the two metals is fairly consistent), and the similarity in physio-chemical behaviour of these group 1 metals. Therefore the correlation between the concentration of these metals reflects the consistency in their volatilisation under incineration conditions.

These data can therefore provide a good reference with which to compare other metal concentrations, as they are believed to be highly dependent on plant operating conditions, and relatively independent of changes in waste charge. Thus, comparison with sodium indicates how much of the variation observed in other concentration profiles is due to bulk conditions, and how much it is due to local conditions, and inhomogeneity in the waste stream.

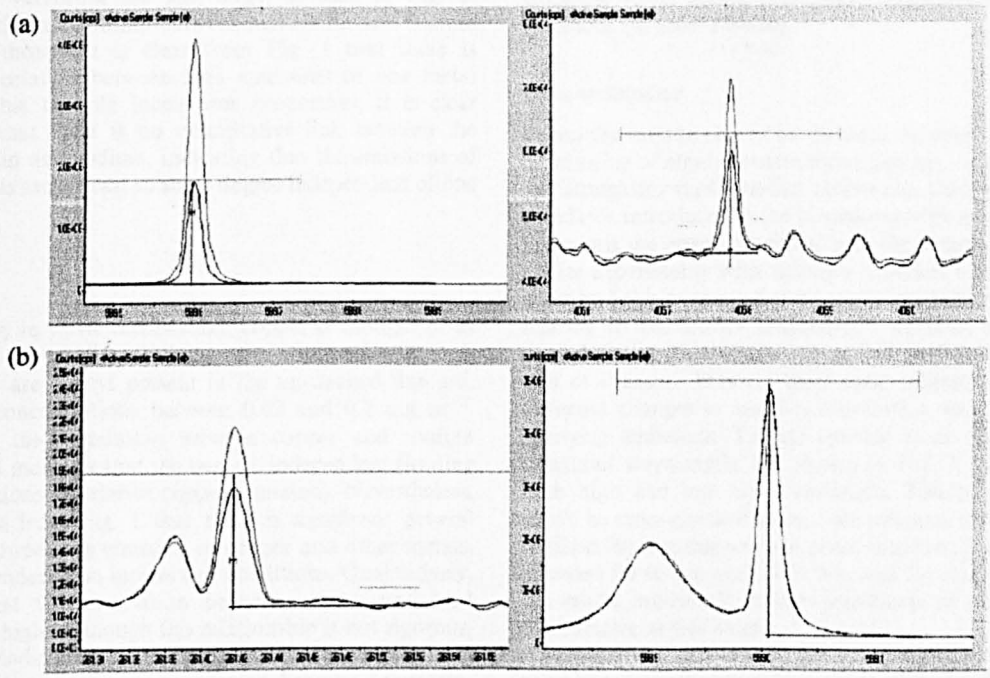

Fig. 5 Selected emission spectrum regions during high and low emissions of different metals. (a) Between 11:36 and 11:44, emission of Na falls substantially. This is shown in the spectrum at the Na I 589.592 nm line, and was confirmed on the Na I 588.995 nm line. At the same time, Pb emission falls, but the change is much smaller. This is the spectrum at the Pb I 405.778 nm wavelength, and was confirmed at the Pb I 261.418 nm wavelength. (b) In contrast, there is a large fall in Pb concentration between 13:01 and 13:05, this time shown on the Pb I 261.418 emission line. The spectrum scans for sodium, at the Na I 588.995 nm line, at the same time shows that Na emission is about constant, with the final change in concentration being due to changing flow between the two measurements. The trends shown were again confirmed on the alternative emission lines.

Lead

Compared with the consistency in relative concentrations of sodium and potassium, most metals show greater and apparently random variation. Such variation is not explicable by changes in bulk incinerator conditions alone, but also by the changing availability of the metal in the waste feed. Typical of such behaviour is lead, which is still found at a high concentration in the un-cleaned flue gas (typically around 0.3–1.0 mg m^{-3}), but with significantly more variation over a time-scale of several minutes to hours, compared with sodium. This is seen clearly in Fig. 2, where the relative emission of lead varies far more with time than the relative emission of potassium.

For sodium, the emissions between 12:00 and 13:30 are broadly similar, with the usual fluctuations. In contrast, lead emissions are noticeably relatively high between 13:00 and 13:30, whereas between 12:00 and 12:50, concentrations of lead are low. These "high" or "low" lead regions, typically lasting around 30 min, are presumed to be due to variation in lead content in the feed waste, with different wastes being fed during the monitoring period. The greater variation in lead concentration compared with sodium agrees well with what is known about the distribution of lead in the waste charge, as it tends to be concentrated in "bulk" items (for example, waste electronics), and is therefore expected to be less evenly distributed in the waste charge.

However, Fig. 1 shows that there is still correlation between plant temperature and lead content, and a fairly strong correlation between periodic variations in oxygen concentration and lead concentration. This suggests that the flue concentration of lead is dependent on furnace oxygen, which is not unexpected, given that PbO is though to be a significant species in lead volatilisation.

Tin

Although the concentrations of tin are relatively low compared with the metals already discussed (0–0.2 mg m^{-3}), the temporal variations are still large, as seen in Fig. 1. Fig. 3 shows the relationship between relative tin and sodium emissions. Although it is clear from Fig. 1 that there is a general association between high emissions of one metal and others (due to bulk incinerator properties), it is clear from Fig. 3 that there is no quantitative link between the emissions of tin and sodium, indicating that the emissions of different metals are at least to some degree independent of one another.

Copper

Conventionally in waste combustion, copper is thought of as a non-volatile metal. Fig. 1 shows that measurable quantities of copper are always present in the un-cleaned flue gas, with typical concentrations between 0.02 and 0.2 mg m^{-3}. Fig. 3 shows the correlation between copper and sodium emissions, and indicates that the two are independent (leading to large variations in relative copper emission). Nevertheless, it can be seen from Fig. 1 that there is significant general association between the emission of copper and other metals, reflecting dependence on incinerator conditions. Qualitatively, it appears that the correlation between copper and lead is particularly high. Although this relationship is not rigorous, due to the periodic changes in lead content of the waste feed, it is thought that short-term correlation between concentrations of these two metals may be high due to specific waste sources which contain both these elements in fairly constant proportion, and possibly chlorine, which would favour the volatilisation of both of these elements (as $PbCl_2$ and CuCl).

Cadmium

Compared with the concentrations of relatively abundant volatile metals examined so far, the concentration profiles for trace volatile metals such as cadmium are quite different. These metals tend to be seen in far better resolved peaks, which appear at random time intervals, and appear independent any other process conditions.

The concentration profile for cadmium is shown in Fig. 4. The "baseline" concentration of cadmium in the flue gas is near-zero, but occasional significant peaks are seen. These are thought to correspond to the presence of occasional discrete sources of cadmium in the waste feed, probably primarily in nickel–cadmium batteries. Cadmium is a highly volatile metal, and it is expected to be completely volatilised in the incinerator. Thus it is assumed that each discrete peak corresponds to a point cadmium source reaching the incinerator, and being rapidly and completely volatilised.

Given that the measured concentration of cadmium in the flue gas and the total volume flow rate have been measured, the total mass of metal accounted for in the flue gas (as vapour or small particulates) for a given time can be calculated thus:

$$M_m = \sum_{T=0}^{T=1} C_m x F_{NTP} \qquad (2)$$

where M_m is the total mass of metal (mg), $T = 0$ is the start of the period (min), $T = 1$ is the end of the period (min), C_m is the measured concentration of the metal at normal temperature and pressure (NTP) (mg m^{-3}) and F_{NTP} is the gas flow at NTP (m^3 min^{-1}).

An individual peak was calculated to correspond to up to about 1 g of cadmium metal. For a 4 hour measuring period, the total mass of cadmium accounted for was 4.47 g, with 2.63 g of this being accounted for during the 6 clearest peaks, over a period of 26 min. Thus, 59% of the cadmium in the flue gas was volatilised in 11% of the time, indicating that temporal variation in concentration is significant. This provides clear evidence that removing specific discrete sources of that metal from the waste stream could have a significant effect on the emissions (to solid residue).

Data verification

Given the unique nature of the data obtained by continuous monitoring of highly contaminated flue gas, data verification is not straightforward. On-line calibration checks with aqueous standards introduced in the laboratory were good, but this did not assess the error associated with the sample line (although earlier experiments with mercury injection in a furnace have addressed this to some degree, while not fully resolving issues relating to particulate transport).[31] Spectral scans were recorded during the monitoring period, and periodic examination of emission lines on these scans helped to confirm that observed changes in metal concentration were indeed due to changing emissions. Typical spectral scans for some of the measured wavelengths are shown in Fig. 5, during times of both high and low metal emissions. Ideally, all the results would be cross-checked against the reference method (US EPA Method 29), but this was not possible at the time, although it is intended for future work. For this, and the other reasons given, the results presented are best considered as being only semi-quantitative at this stage.

Nevertheless, the results obtained from this study are in good broad agreement with existing data in the literature, for the analysis of small particulates and bulk bag-filter residue from waste incineration. These results can be compared by taking the ratio of one volatile metal to another, as shown in Table 2. Lead is used as a reference metal, and it is seen that for the volatile metals, agreement is fair for most, given the

Table 2 CEML data verification—comparison of metal concentration ratios (with respect to lead) in flue gas, small particulates and flue gas clean-up residue

	CEML average concentration/ mg m^{-3}	CEML concentration with respect to lead	Particulates <2 μm[32]	Incinerator flue gas clean-up residues[35]
Cadmium	0.0113	0.022	0.011	0.024
Copper	0.0757	0.15	0.021	0.069
Lead[a]	0.496	1	1	1
Potassium	7.14	14		1.9
Sodium	3.57	7.2	1.0	2.1
Tin	0.104	0.21	0.11	0.11

[a] By definition, given calculation method.

differing nature of the samples, the different plants being studied, and the differing ages of the work (with associated changes in expected waste composition). The fact that the CEML values are generally higher may indicate that the solids analyses were not totally effective at capturing the smallest particulates/vapours of the most volatile metals, or dissolving them for liquid analysis. For sodium and potassium, the relative amounts of these metals with respect to lead is unusually high, indicating that more is found by the CEML in vapours and particulates less than 10 μm than might be expected. However, this is reflected in analyses we have done on residues from the same plant, which show that unusually large amounts of Na and K tend to transfer to the air pollution control device (APCD) residue, suggesting that this is due to the operation of this particular plant.[34]

Detection limits

Given the variations in signals, which are known to be introduced by the changing gas matrix, particularly in the real system, a theoretical detection limit from the calibration procedure is hardly a useful indicator of practical detection limit. The rather pragmatic solution proposed by the authors for this highly unusual matrix is therefore as follows. Limited on-line monitoring of cleaned flue gas, beyond the bag filters, was conducted for about 6 hours. Although some small amount of metal may be present in this situation, compared with the high concentrations found in the un-cleaned gas, this effectively represents a blank signal for metal in the gas matrix in which measurements are made. Detection limits are therefore assumed to be 3σ of the measurements for a 6-hour period in the flue gas, and lead to the detection limits shown in Table 3. Given the challenging analytical matrix, these figures are reasonable, and in most cases, measured metal emissions (certainly during peaks) are well above this detection limit, showing that the analytical system is fit for the intended purpose.

Table 3 Detection limits in un-cleaned flue gas/mg m^{-3}

Element	Detection limit/mg m^{-3} (3σ)
Cadmium	0.007
Copper	0.007
Lead	0.014
Potassium	0.089[a]
Sodium	0.064[a]
Tin	0.018

[a] Probably an over-estimate, due to measurable concentration of analyte in the assumed "blank".

Conclusions

From the results of this study, the following can be concluded.

- Unique, semi-quantitative on-line measurements can be made in the highly contaminated, untreated flue gas of a waste-to-energy plant.
- Continuous measurements give a unique insight into the temporal variation in metal concentrations in the un-cleaned flue gas from a waste-to-energy plant.
- Individual events in the metal concentration profile can be visualised, and linked to the factors responsible in a unique manner, proving the importance of time-resolved measurements.
- Such measurements could provide feedback to pollution control devices, optimising emissions control.
- A number of operational variables are important in determining metal volatilisation. Incinerator temperature and oxygen are important, as is the concentration of metal in the waste.
- Local conditions within the combustion chamber (non-equilibrium situations) may also affect metal behaviour though these cannot readily be measured.
- The results for cadmium are environmentally significant as they indicate that removal of specific sources of this metal from the waste stream would cut concentrations in the system to near-zero, a highly desirable environmental target.
- In general terms, metals may be classified into 3 broad categories:

1. Volatile bulk metals, such as sodium, which are present in most feed waste, and where concentration variation in the flue gas is largely due to changes in the combustion conditions;
2. Volatile bulk metals with uneven distribution in the waste (often found in bulky wastes), such as lead, which are present in high concentration, but show more overall temporal variation than the more evenly distributed metals;
3. Volatile trace metals, such as cadmium, which are present only occasionally in the feed, and lead to occasional random peaks in an otherwise near-zero concentration profile

Thus, the measurements obtained of metal concentrations within the flue gas of a waste-to energy plant have provided an insight into how metals behave during waste combustion. Such on-line measurements will be invaluable in optimising waste handling strategies to minimise the impact of pollutants in the waste stream, a highly desirable environmental target.

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IDENTIFICATION OF METAL POLLUTANT SPIKES IN MUNICIPAL SOLID WASTE INCINERATORS BY CONTINUOUS ON-LINE ANALYSIS
(AS SUBMITTED TO "WASTE MANAGEMENT", APRIL 2005)

D Poole, V Sharifi, J Swithenbank, Sheffield University Waste Incineration Centre (SUWIC), University of Sheffield, Mappin Street, Sheffield, S1 3JD, UK*

B Argent, Dept of Engineering Materials, University of Sheffield, Mappin Street, Sheffield, S1 3JD, UK

D Ardelt, Spectro AI, Bochstrasse 10, D-47533 Kleve, Germany

Abstract
SUWIC's unique mobile metals emissions monitoring laboratory has been used to provide data on the metal pollutant spikes in the flue gas from a municipal solid waste incinerator, prior to gas clean-up. The laboratory has a flexible heated sampling probe that extends 40m into the plant, allowing the simultaneous on-line measurement of the concentrations of more than 30 metals by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES). As little is known about temporal variation in metal volatilisation, this is therefore seen as a major advance.

It has been shown that variation in metal concentration is significant, and is correlated both to plant operating conditions, and other factors. The results demonstrate that there are large spikes of vaporized cadmium and mercury, which are believed to be due to fluctuations in the waste feed material. These could be minimised through a combination of careful process control and the removal of specific sources of these metals from the waste stream.

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* Email d.poole@sheffield.ac.uk, Tel +44 (0)114 2227555, Fax +44 (0) 114 2227501

The study shows that the elemental loading is far from uniform, and that as such the point concentrations may be far higher than are conventionally expected, which is significant for those seeking to model metal behaviour in combustion, and those designing pollution control devices.

Key Words
Municipal waste incineration, heavy metals, pollutants, ICP-OES, On-line analysis.

Scientific Background
Following extensive research, much is known about the combustion process, formation of pollutants and pollutant removal or impact minimisation. Waste to Energy plants now provide a highly sophisticated and controlled waste processing system (2000, Abad et al., 2002). However, compared with the wealth of research into bulk pollutant control, and trace organic pollutants, far less is known about the behaviour and distribution of toxic volatile metals in the incineration process (Evans and Williams, 2000).

At present about 7% of UK controlled waste is incinerated, with recovery of heat energy through electricity generation, and/or district heating schemes, and the proportion of waste incinerated is set to increase, under current government recommendations (DEFRA, 2000). Incinerator operating conditions are tightly controlled, so if operating within legislative limits, incineration is a relatively clean process for the disposal of waste, where none of the available options are ideal (Williams, 1998). Current EC legislation limits permissible pollutant levels in gases, liquids, and solids resulting from incineration. These regulations require the continuous measurement of bulk pollutant constituents, such as SO_2, HCl and dust, and extractive sampling of trace metal and organic pollutants. This legislation indicates that it is the intention of regulatory bodies to introduce continuous monitoring of metals, as soon as adequate technology becomes available (Bastian and Lambert, 2000).

Extractive monitoring methodologies (such as US EPA Method 29) require the taking of discreet samples with subsequent laboratory based analysis of the filters and contaminated impinger solutions obtained. This gives a single value for metal

emissions, typically once every six months, and averaged over between 30 minutes and 8 hours. Consequently, there is no information on emission variation within that time, or of possible emission events outside of that monitoring period. The development of real-time monitoring of metallic pollutants in gaseous samples is therefore seen as a major breakthrough in both the understanding of industrial processes and in the measurement of emissions for legislative purposes. Continuous monitoring allows plant emissions to be checked at all times, with the potential to provide control feedback, should the emissions limits be exceeded, and allows operators to demonstrate that their process is operating cleanly at all times. In terms of monitoring in-process flue gases, prior to flue gas treatment, continuous monitoring shows how metal concentrations vary with time, and are linked to plant operating conditions, and variations in waste feed, and hence lead to a variable load on the flue gas clean-up system. This information is vital in developing strategies to optimise flue gas treatment, and minimise the impact of metal pollutants (Belevi and Moench, 2000, Morf et al., 2000, Wendt, 1994).

One of the major reasons for expecting that metal concentrations in the flue gas will vary with time is the fact that the waste feed is extremely heterogeneous (Williams, 1998), and as such, metal concentrations in the fuel will vary significantly over a relatively short time period (Morf et al., 2000). Ideally, the composition of the waste entering the process would be well known for test experiments, but in practice it is impossible to obtain accurate analysis of the waste entering a commercial scale incinerator, along with realistic estimates of its inhomogineity (Van Der Sloot et al., 1997). This very inhomogeneity will affect the way that the waste burns on the incinerator grate, as the burning bed itself is far from uniform (Yang et al., 2002), and so experiments with better characterised, more uniform fuels will never completely mimic the actual processes going on in a full-scale municipal waste incinerator. In fact analysis of the composition of incinerator by-products is probably one of the better indicators of the changing composition of the fuel (Morf et al., 2000), and on-line monitoring of these is the only realistic way of determining how changes both in feed and operating conditions affect the composition of flue gas of a full-scale waste combustor on a minute-by-minute basis.

Experimental Continuous Emissions Monitoring (CEM) techniques for flue gases began appearing in the literature in the mid-1990's (Nore et al., 1993, Trassy and Diemaizonek, 1994, Meyer and Lee, 1994, Seltzer and Green, 1994). Previously, there had been very little by way of multi-element continuous monitoring which may have been applicable to gaseous emissions from industrial processes. Despite the advances in such techniques, none have been found to meet the quality requirements for regulatory endorsement (Lemieux et al., 1998, Woskov et al., 2000, Hill et al., 2002). Recent developments in end-of-pipe monitoring technologies have either been in laser or microwave induced plasma techniques (Hill et al., 2002, Buckley et al., 2000, Woskov et al., 2000), or in Argon-ICP-OES (Hassaine et al., 2001, Seltzer, 2000). Cooper (2004) is developing an end of pipe monitoring system, based on XRD, but this will only make one measurement about every 20 minutes. While this is perfectly acceptable from a legislative monitoring perspective, it does not fulfil the demands identified here for information on rapid temporal variations in signals for system diagnostic purposes.

Although there have been numerous continuous emissions monitoring systems developed experimentally, the main problems encountered in continuous monitoring of flue gases are common to most of them. These relate to maintaining adequate reliability and sensitivity in an unusual, variable, and difficult matrix (Trassy, 1996). These problems broadly fall into two categories: Firstly, sample integrity is difficult to maintain, due to problems of particulate deposition on the sample probe, which tends to lead to measurement drift and poor repeatability (British Standard 3405, 1983). Secondly, the changing bulk sample matrix (in particular interferences from bulk gases such as CO_2), tend to cause changes in instrument sensitivity, which lead to poor precision unless carefully accounted for (Seltzer and Meyer, 1997, Seltzer, 1998, Trassy and Diemaizonek, 1994). Despite these difficulties, we have shown that minute quantities of toxic metal can be quantitatively detected in real combustion systems with our mobile laboratory, within the ±20% demanded of CEM technologies (Clarkson et al., 2004).

Previous work by Belevi and Moench (2000), Law and Gordon (1979), and Greenberg et al., (1978) have identified the means by which different metals transfer to the flue gas, the former by examining the concentration ratio of the metals found in residues from different parts of the boiler system, and the latter two by measuring

bulk fly ash residue composition, and comparing it with the composition of small particles. In addition, they also attributed differing metal transfers to the gas phase to the physical nature of the waste – classifying each metal as being mainly found in bulk [non-combustible] waste, non-bulk [combustible] waste, or both. This data provides a useful comparison for the CEML data obtained, and a summary is given in Table 1. A good summary of the physical and chemical processes involved in metal partitioning in incinerators is given by (Linak and Wendt, 1993). Species transferred by an evaporation/condensation route are found to be enriched in the smallest particles in the flue-gases, as well as in the vapour phase (Davison, 1974, Greenberg et al., 1978). As the CEML is unable to accurately analyse particles greater than 10μm, measurement accuracy will be best for the more volatile metals.

Experimental

Analytical System

Data was obtained using a state-of-the-art mobile Continuous Emissions Monitoring Laboratory (CEML) using ICP-OES detection. This unique system, built in collaboration with SPECTRO A.I. (Kleve, Germany), is a self-contained laboratory that is designed to be used at industrial locations for the measurement of gaseous emissions. This equipment has previously been described in detail (Clarkson et al., 2003), but briefly, it comprises of a 40m heated sampling line, isokinetic sample interface, and a state-of-the-art ICP-OES-CCD spectrometer, capable of making simultaneous quantitative measurements of over 30 elements, each on multiple emission lines as required.

The main ICP operating parameters used at the plant trials are given in Table 2. Some of the monitored emission lines are given in Table 3. One measurement per minute was made using the equipment.

The Test Site

The test site selected for this work was a mass-burn municipal solid waste incinerator (MSWI) plant. A schematic diagram of the plant is shown in Figure 1. Although full analysis of the incoming waste was effectively impossible without perturbing the nature of the "normal" waste feed (Van Der Sloot et al., 1997), typical literature values for municipal waste composition in Europe, with an indicator of sampling variations experienced between 2 hour samples, are given in Table 4. Nevertheless, it should be noted that national, and seasonal variations may be expected, meaning that this analysis is only an indicator of what may be expected in the waste feed.

The plant has 2 lines, each incinerating up to 12 tonnes of waste per hour, with an average throughput of approximately 10 tonnes per unit per hour. The grate type is reverse reciprocating, and the furnace walls are water cooled, providing heat to the energy recovery system. During our tests, furnace temperature was measured using two thermocouples, one on either side of the furnace, with operational parameters being changed to maintain the temperature between 850°C and 1100°C. The plant was operated with excess air, leading to an oxygen level in the combustion chamber between 6% and 14%, measured in the radiation shaft. The combustion chamber is followed by the energy recovery boiler, and an economiser, resulting in a final flue gas temperature after the economiser averaging 130°C.

Flue gas treatment comprises of a dry scrubbing system using hydrated lime to control acidic gas emissions, and activated carbon to trap heavy metals and organic micro-pollutants. Fabric filters are used to collect the fly ash and scrubber products, and are designed to remove particulate matter down to a minimum of 5μm. The emitted flue gas was continuously monitored beyond the fabric filter by the plant operator, for temperature, and concentrations of CO, SO_2, NO_x, HCl, O_2, H_2O, and dust.

After the economiser, and before the sorbent injection of the flue gas clean-up system, there was a standard 4" BSP sampling port in a vertical section of ducting, which was used in this work. The sampling location is indicated on the schematic diagram, Figure 1. The CEML sample train was connected to the sample port, at which point the ducting measured about 0.9m x 0.9 m, and continuous on-line emission monitoring of un-cleaned flue gas was undertaken.

Sampling Considerations

Achieving reliable analytical measurements in the un-cleaned flue gas was

extremely challenging, despite a wealth of information already obtained on optimising the laboratory for clean flue-gas monitoring during previous on-site monitoring at the same plant (Clarkson et al., 2003). The un-cleaned gas provided an extremely difficult analytical matrix, with very high particulate loading, and very high and variable concentrations of a number of metals, along with trace concentrations of others. The heated sample line and analytical instrument was designed for sampling of small particulates and gases, with particle sizes not over 10 μm, so the sampling train employed at the plant end of the line included a cyclone designed to remove larger particulates, as well as a probe tip to ensure isokinetic sampling (British Standard 3405, 1983). As it was not our aim to sample large particulates, a traverse of the stack was not required, and the sampling tip was kept approximately central in the ducting throughout the experimental programme.

In addition to the data collected using the CEML, the measurements made by the plant during the monitoring time were obtained. Data was recorded for furnace conditions (temperature and oxygen), measured at the top of the radiation shaft, and also temperatures of the flue gas before and after the economiser. The full set of emission data, recorded by the plant operator, was obtained for cleaned flue gas, after the bag filters. This was measured in the line 1 ducting, immediately prior to the point where the gases from the two lines meet at the base of the stack. Temperature, oxygen content, moisture content and flow rate measurements made here, along with the temperatures at the CEML sampling point were used to normalise the CEML results to standard reference conditions (273 K, 1 Atmosphere, 11% oxygen, dry gas) (European Community Legislation, 2000). Other data obtained was used to show how metal emissions correlated to changes in plant operating conditions. In order to simplify comparison of data from different sources, one value was used per minute, corresponding to the measurement time of our instrument. Where more data points were recorded by other instruments, the last data point within that minute was used.

Results and Discussion

The concentrations of volatile metals in flue gas prior to cleanup were generally found to be extremely high, and dependent both on plant conditions, and the changing nature of the waste charge supplied to the incinerator. For a better understanding of the factors which lead to metal volatilisation, and the temporal variations in the process, not only are new experimental data required, but also physio-chemical explanations of the results, and correlation with bulk plant conditions. Thermodynamic models predicting volatility of metals in the combustion system are currently being developed by the authors (Poole and Argent, 2004), building on existing work on municipal waste combustion by numerous researchers, including Linak and Wendt (1993), Fernandez et al. (1992), and Wu and Biswas (1993). The latest initial results from this study were used to explain some of the trends in the experimental results. Measured concentration profiles for different metals are shown below. Given that the experimental system necessarily excluded the sampling of large particulates, and some limited problems were experienced with unwanted sample deposition, the results are best considered as semi-quantitative indicators of metal concentrations in the flue gas. Occasional gaps in the measured metal emissions are due to unavoidable interruptions to the measurements, to allow emptying of the sampling cyclone, and cleaning of the sample probe to remove any particulate depositions, although deposition in the heated line was minimal.

Sodium

Figure 2 shows a typical concentration plot for the abundant volatile metal sodium, along with the temperature and oxygen measurements made in the combustion chamber. Concentrations vary between about 2 and 8 mg m^{-3}, with emissions generally being low when furnace temperatures are low, and with periodic variations of about 2-3 minutes corresponding approximately to the changing oxygen concentration in the furnace. Oxygen concentration is thought to be an indicator for changing air flow rates, as increased air flow will increase particulate entrainment in the gas phase. Nevertheless, these factors do not fully explain the variation observed, which is also believed to be linked to changing waste characteristics, in particular the availability of either sodium itself, or chlorine, which is thought to have a significant effect on metal volatilisation (Abbas et al., 1996, Poole and Argent, 2004). Local conditions within the combustion chamber may also be significant (eg temperature hot-spots), though these cannot be inferred from the bulk measurements made (Yang et al., 2002). The very high concentrations of sodium measured indicate that there is a large amount of this metal present as vapour or

small particulates, showing that there is a significant evaporation/condensation transport mechanism.

Potassium

Figure 3 shows the concentrations of potassium found in the un-cleaned flue gas, compared with the concentration of sodium. The relative ratio for a metal is obtained by dividing the actual measured concentration at a given point by the average for sodium for the 4-hour monitoring period reported. It can be seen that for most of the monitoring time, the ratio of sodium to potassium is remarkably consistent, at about 1:2. This correlation is attributed to both the wide availability of these metals in the waste, and their similar physio-chemical properties. Sodium and potassium are both important elements in vegetable matter, and as vegetable and garden wastes form a significant part of domestic waste, this contributes to stabilising the Na:K ratio. Thermodynamic calculations predict that the behaviour trends of these two group 1 metals will be very similar, reflecting well-known periodicity trends, though the magnitude of the volatilisation of the two metals is expected to be different, and this is indeed the case (Poole and Argent, 2004). Thus the concentrations of these metals in the flue gas do not merely reflect those in the waste charge, but instead reflects the consistency in volatilisation of the two metals, in incineration conditions. Given the consistency of the data, they can provide a good reference with which to compare other metal concentrations. The concentration of sodium in the flue gas is believed to be highly dependent on bulk plant conditions (certainly for volatilisation, and probably for entrainment), so comparison with this metal can indicate nicely how much of the variation observed in other concentration profiles is due to bulk conditions, and how much it is due to local conditions, and inhomogeneity in the waste stream.

Lead

Compared with the remarkable consistency in relative concentrations of sodium and potassium, most metals show more apparently random variation. Such variation is not explicable by changes in bulk incinerator conditions alone, but is also attributed to changing availability of the metal in the waste feed. For example typical lead concentrations in flue gas are shown in Figure 4. The concentrations of lead in the un-cleaned gas are high, typically around 0.5 – 1.0 mg m^{-3}, more than ten times the maximum permissible emission level for atmospheric discharge, which is effectively ~0.05 mg m^{-3}, as the limit is 0.5mg m^{-3} for the sum of 9 metals (European Community Legislation, 2000). As with other volatile metals, correlation can be seen between periods of low temperature and low lead content, and similarly high temperature and high lead content. Again, periodic variations in oxygen concentration and lead concentration are similar; suggesting that the concentration of lead found in the flue gas is largely dependent on bulk incinerator conditions. This fits with our thermodynamic predictions, which suggest that PbO is a significant volatile species for lead transfer, even in the presence of chlorine (Poole and Argent, 2004).

Nevertheless, compared with sodium, lead exhibits greater overall variation in flue gas concentration with time, on a scale of several minutes to hours. This is seen clearly in Figure 5. For sodium, the emissions between 10:00 and 11:00 and 12:30 and 13:00 overlay well with lead emissions, despite their different relative magnitudes. In contrast, lead emissions are noticeably relatively increased between 13:00 and 13:30, whereas between 12:00 and 12:15, concentrations of lead are particularly low. The concentration of sodium during these four regions is broadly similar.

Using sodium as a "reference", whose concentration in the un-cleaned flue gas is attributed almost entirely to bulk plant conditions, the long-term variations in lead are interesting. The short-term variations correlate well with sodium and potassium plots, indicating dependence on bulk plant conditions. However, the longer-term temporal variations in lead, with general regions of "higher" or "lower" relative lead concentration, typically lasting up to around 30 minutes, must be presumed to be due to variation in lead in the feed waste, with wastes with both relatively high and relatively low lead content being fed during the monitoring period. This implies that the volatilisation of lead is a relatively slow process, implying that reaction kinetics may be significant in metal volatilisation.

The greater variation in lead concentration compared with sodium agrees well with what is known about the distribution of these two metals in the waste charge, with sodium being found in the majority of waste types, but with lead tending to be

concentrated in "bulk" (largely non-combustible) waste. Nevertheless, the observed association between sodium and lead concentrations indicates that the volatilisation of lead is still dependent on bulk incinerator conditions.

Zinc

The concentration profile for zinc is shown in Figure 6. Periodic fluctuations are seen, which correspond somewhat to the fluctuations in plant conditions, with concentrations varying between about 0.5 mg m^{-3} and 2.5 mg m^{-3}. Once more, the metal concentrations prior to the bag filters are very high.

It is generally seen that at times when either (or both) furnace temperature measurements are low (eg 09:50, 10:13-10:17, 11:45, 12:05), concentrations of zinc soon after are low. It is assumed that the largest zinc peaks are not due only to process conditions, but also to specific sources of the metal in the waste feed, leading to high concentrations of zinc in the un-cleaned flue gas. Such peaks in the concentration-time profile are seen between 10:40 and 10:50, and 12:15 and 12:30.

Figure 7 shows a comparison between the relative concentrations of zinc and sodium, and it is once more seen that most of the time, correlation between the concentrations of the two metals is good, particularly for example between 09:30 and 10:30, and again between 13:00 and 14:00. This comparison emphasises the independence of the zinc peaks at 10:40-10:50 and 12:15-12:30 from the emissions of other metals, reinforcing the supposition that they are a result of changing waste feed, rather than plant conditions.

It is interesting to note certain features of the three most dominant peaks observed in Figure 7, which are spikes in zinc concentration at 10:40-10:50 and 12:15-12:30, and a spike in sodium concentration between 11:30 and 11:40. It can be quite clearly seen that each of these peaks comprises of a general region of high concentration of the spike metal, but with one or more dips within the peak, giving it a more complex secondary structure than a single peak. At the point where the concentration of the "dominant" metal drops, the concentration of the other bulk volatile metals tends to increase, suggesting that the volatilisation process is complex, with the concentration of one metal in the gas phase affecting the concentration of another, due to the complex equilibrium established between all the volatile components in the system. It is possible that "total metal" volatilisation is being limited by the availability of non-metallic reagents such as chlorine, as most metals chlorides are more volatile than the "native" metals (Linak and Wendt, 1993). Previous thermodynamic predictions (Delay et al., 2001) predicted that in clinical waste incineration, increasing S:Cl ratio inhibited the volatilisation of both zinc and sodium, and that with a constant S:Cl ratio, increases in Na concentration inhibited Zn volatilisation. Such an explanation could explain the observed results, and would indicate a dependence on chlorine/sulphur availability.

Cadmium

Compared with the concentrations of relatively abundant volatile metals examined so far, the concentration profiles for less common, volatile metals are quite different. Whereas for bulk metals, regions of high or low concentration of a particular metal last for up to 30 minutes and are clearly influenced within that time by the changes in the bulk incineration conditions and the concentration of other bulk metals, the trace volatile metals tend to be seen in far better resolved peaks, which appear approximately independent any other process conditions.

The concentration profile for cadmium is shown in Figure 8. Unlike the more abundant heavy metals, the baseline concentration of cadmium in the flue gas is near-zero (typically less than 0.03 mg m^{-3}, which is lower than the allowable emission limits, even before clean-up), but occasional significant peaks are seen. These peaks are not correlated to plant events, and are thought to correspond to the inclusion of occasional discrete sources of cadmium in the waste feed, probably primarily in nickel-cadmium batteries (Linak and Wendt, 1993). Cadmium is a highly volatile metal, and it is expected to be completely volatilised during combustion (Delay et al., 2001). Thus it may be reasonably assumed that each discrete peak corresponds to a point cadmium source reaching the incinerator, and being rapidly and completely volatilised.

Given that the measured concentration of cadmium in the flue gas and the total volume flow rate have been measured, this information can be used to calculate the total mass of metal accounted for in the flue gas (as vapour or small particulates), as

shown:

$$M_m = \sum_{T=0}^{T=1} C_m F_{NTP} \qquad (1)$$

Where M_m is the total mass of metal accounted for (mg)
T=0 is the start of the calculation period (min)
T=1 is the end of the calculation period (min)
C_m is the measured concentration of the metal at NTP (mg m^{-3})
and F_{NTP} is the measured flow of gas for this period at NTP (m^3 min^{-1})

An individual peak was calculated to correspond to up to 1g of cadmium metal. For example, the peak between 10:06 and 10:11 is calculated to correspond to 0.65g cadmium. For a 4 hour period on 20/07/04, the total mass of cadmium accounted for in the flue gas is 4.47g, with 2.63g of this being accounted for during the 6 clearest peaks, over a period of 26 minutes. Thus 59% of the cadmium in the flue gas is accounted for in 11% of the time, indicating that the temporal variation in concentration is significant.

Mercury

Figure 9 shows the concentration profile for mercury, another volatile trace metal. Once more, the baseline concentration for most of the measurement period was near zero, with few occasional peaks. The black arrow on the plot indicates the addition of a instrumental calibration check standard, which was added during the run, and was found to be quantified at 108% of expected value, indicating good instrumental quantitation accuracy. Prior to this, a series of extremely large mercury concentration peaks are seen, for a 1.5 hour period. This event was the only such one seen during the week, and is thought to be extremely unusual, with the remainder of the measuring time showing only baseline mercury concentration, with occasional small peaks, lasting one or two minutes, and being up to 0.2 mg m^{-3} in the un-cleaned flue gas. The mercury in the flue gas in the 1.5 hour period between 12:50 and 14:20 was calculated to correspond to the addition of about 90g of mercury to the furnace, an extremely large single amount for a metal whose use is strongly discouraged. This quantity of metal could occur in municipal waste, for example, through the disposal of an old barometer, or several thermometers, but it is emphasised that the occurrence of such events is believed to be extremely low, and only one such event was witnessed during a week of monitoring of the plant.

Given the high volatility of mercury, it is surprising how long the emission for mercury lasts, and implies that even for such a volatile metal, local bed conditions and reaction kinetics significantly affect volatilisation. However, care should be taken with inferences drawn, as such a large peak of mercury may induce a "memory" effect, both in the analytical system, and possibly in the boiler system.

Observation of such an event highlights the importance of continuous monitoring. It is extremely unlikely to have been observed by any other means, and provides reassurance that aside from such unusual events, the concentrations of mercury are extremely small. Given the highly unexpected nature of this observed result, the CEML data was carefully checked, with examination of the emission spectrum in the region of the emission line, and confirmation on three other mercury emission lines. These checks confirmed that the signals observed were unambiguously due to mercury, and not to any kind of spectral interference.

Calcium

The concentrations of non-volatile metals observed in incinerator flue gases, as vapours or particulates smaller than 10 μm are extremely small, in most cases below a realistic detection limit for the conditions encountered. For example, chromium, cobalt and vanadium were all observed at baseline (zero) concentration throughout continuous monitoring, so the profiles for these metals are not shown. Any observable variation is evidently due to changing gas matrix rather than true signal variation.

Nevertheless, bulk non-volatile metals such as calcium can be detected, and a concentration plot for calcium is shown in Figure 10. In general there is less overall temporal variation in the calcium profile than for the more volatile metals.

Nevertheless, there is a strong association between measured calcium concentration and oxygen level in the combustion chamber, with high calcium nearly always being accompanied by high oxygen (though sometimes there is an apparent time mismatch, due to the differing measurement periods on plant and in the lab). This supports the theory that calcium is mainly transferred to the flue gas by particulate entrainment, which will be enhanced by increased air flow in the combustion chamber. The fact that the calcium profile does not correlate exactly with the oxygen plot indicates that air flow is not the only factor involved in entrainment, and presumably further variation is introduced by the different availability of "entrainable metal" in the waste feed.

Compared with the composition of solid residues from flue-gas clean-up, the concentrations of calcium are very low, relative to the concentration of volatile metals observed (aside from the complication of lime addition). This fits with what is known about enrichment of volatile metals in the smaller particles, because of the metal transport mechanisms involved. It should therefore be emphasised that the measured concentrations of calcium represent the concentration in the smallest size fraction of particles in the flue gas, not a "total" analysis of the dust/grit in the gas stream. Nevertheless, the results are highly interesting, and indicate the effect of changing combustion chamber air flows on the entrainment of non-volatile metals.

Data Verification

Given the unique nature of the data obtained by continuous monitoring of highly contaminated flue gas, data verification is not straightforward. Ultimately, comparison of our analysis with the reference method (US EPA Method 29) would be desirable, although this has not been possible to date. However, the results obtained from this study are in broad agreement with literature data for the analysis of small particulates and bulk bag-filter residue from waste incineration, as shown in Table 5. These results show the ratio of one volatile metal to another, in order to allow comparison between different data sources. Lead is used as a reference metal, and it is seen that for the volatile metals, agreement is fair for most, given the differing nature of the samples, the different plants being studies, and the differing ages of the work (with associated changes in expected waste composition). For example correlation is good for Cd, Hg, Sb, and Zn between CEML data and concentrations found on small particulates, or in bulk APC residues. The fact that the CEML values are generally higher may indicate that the solids analysis were not totally effective at capturing the smallest particulates/vapours of the most volatile metals. For sodium and potassium, the relative amount of these metals with respect to lead is unusually high, indicating that more is found by the CEML in vapours and particulates less than 10μm than might be expected. This apparent anomaly is introduced by the fact that although these metals are transported by evaporative routes, they are known to be deposited significantly in the latter parts of the boiler system (Belevi and Moench, 2000). Therefore, the fact that the CEML measurements are made at an earlier point in the boiler system will significantly increase the amount still found as vapour or on measurable particulates, compared with the "later" solids analyses. This anomaly further reflects and helps to explain the differing information in the literature about the behaviour of sodium, which was discussed in the scientific background to the paper.

For the relatively non-volatile trace metals Ba, Co, Cr, Mn, the concentrations measured by the CEML are generally under the detection limit of the analytical system. This result is actually in good agreement with the other data, which all indicates extremely small concentrations of these metals in the solid residues. For non-volatile metals such as Ca and Fe, much greater concentrations are seen in the MSWI residue data than the CEML data or particulate information, reflecting the expected trend that these metals are present as larger particulates, and agreement between CEML data and small particulate analysis is much better.

Detection Limits

Due to the effect of the changing flue gas matrix on the sensitivity of the analytical instrument, an instrumental detection limit, calculated during the calibration of the instrument, does not give a realistic assessment of the lower concentration limit which may be detected by the instrument. The authors have developed an alternative method, based on measurements of flue gas from the plant, beyond the clean-up devices, which was known to contain metals only in extremely small concentration, and could thus be considered as a blank signal for the purposes of system calibration (Clarkson et al., 2003). Although small concentrations of metal may still be present in this gas, it effectively provides a realistic calibration blank.

Detection limits were calculated as three times the standard deviation of the (blank) signal measured in the cleaned flue gas for a 5 hour period, as given in table 6 . Given the magnitude of the signals seen for most metals in the un-cleaned gas, it is seen that the detection limits are adequate, usually being considerably lower than the measured signals. The extremely good baseline resolution for these signals, which leads to low standard deviation, indicates that the instrument is highly sensitive, and provides further confirmation that measured signals in un-cleaned gas are due to changing metal concentration, rather than to matrix changes.

Conclusions

This paper has presented unique, semi-quantitative temporally resolved data which we obtained for metal concentrations in the vapour and small particulates in the flue gas from a municipal waste incinerator. From this successful research, it is concluded that:

- Time resolved continuous measurements give a unique insight into the temporal variation in metal concentrations in the flue gas from a large scale municipal waste incinerator, prior to flue gas treatment.
- Significant variation in metal concentrations with time has been seen, demonstrating the importance of time-resolved measurements
- Individual events in the metal concentration profile have been visualised, and linked to the factors responsible, in a way which has hitherto been impossible.
- It is seen that in a real waste combustion system, a number of operational variables are important in determining metal volatilisation, and subsequent concentration in small particulates and vapours in the un-cleaned flue gas. Incinerator temperature and oxygen (flow) are shown to be important, as is the concentration of metal in the waste, which is inferred from observed arbitrary variation in metal concentrations, which is not attributable to any other factor.
- The work suggests that the combustion chamber is indeed a highly complex system, with different factors appearing to dominate metal concentrations at different times.
- In general terms, the results for different metals may be classified into 4 broad categories:
  - Volatile bulk metals, such as sodium and potassium, which are present in most feed waste, and where concentration variation in the flue gas is largely due to changes in the combustion conditions
  - Volatile bulk metals with uneven distribution in the waste (often found in bulky wastes), such as lead and zinc, which are present in high concentration, but show more overall temporal variation than the more evenly distributed metals
  - Volatile trace metals, such as cadmium and mercury, which are present only occasionally in the feed, and lead to occasional random peaks in an otherwise near-zero concentration profile
  - Non-volatile metals, such as calcium, which are transported largely by entrainment of large particles, for which the CEML measurements of vapour and small particulates do not accurately reflect the true metal content.
- The data obtained from this study will be used to develop, test, and refine thermodynamic models of metal behaviour in the combustion system. This work is currently underway. Thus the experimental work reported here will prove invaluable in developing understanding of the processes which cause metal concentrations in flue gas to change with time, and therefore how changes to the incineration system could improve the environmental impact of what is already a highly sophisticated waste management system.
- The results observed for cadmium and mercury are highly significant from an environmental point of view, as they indicate that diversion of certain specific "point" sources of these metals from the incinerated waste stream would cut concentrations of these metals in the system to near-zero, a highly desirable environmental target. This could be aided by improved collection and recycling facilities. There is also indication that careful control of process conditions could be used to determine the partitioning of other volatile metals, either to minimise volatilisation, or to concentrate volatile metals in the small particles in flue gas, which could potentially be segregated, and used as a feedstock for metal recovery.

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Table 1 Sources and Major Transfer Mechanisms of Metals in MSW Incineration (summarised **from** (Belevi and Moench, 2000)

Metal	Major Transport Mechanism	Sources in Waste
Si	Entrainment	Bulk items [non-combustibles]
Fe	Entrainment	Bulk items [non-combustibles]
Co	Entrainment	Bulk items [non-combustibles]
Cr	Entrainment	Bulk items [non-combustibles]
Mn	Entrainment	Bulk items [non-combustibles]
Al	Entrainment	All
Ca	Entrainment	All
Mg	Entrainment	All
Na	Entrainment*	All
Ba	Entrainment	All
Ti	Entrainment	All
K	Both	Non-bulk items [combustibles]
Cu	Evaporation / Condensation	Bulk items [non-combustibles]
Mo	Evaporation / Condensation	Bulk items [non-combustibles]
Pb	Evaporation / Condensation	Bulk items [non-combustibles]
Sn	Evaporation / Condensation	Bulk items [non-combustibles]
Zn	Evaporation / Condensation	Bulk items [non-combustibles]
Sb	Evaporation / Condensation	Non-bulk items [combustibles]
As	Evaporation / Condensation	Non-bulk items [combustibles]
Cd	Evaporation / Condensation	Non-bulk items [combustibles]
Hg	Evaporation / Condensation	Non-bulk items [combustibles]

* Although the evidence presented by Belevi and Moench suggests transport by entrainment, other work (eg (Greenberg et al., 1978) provide contrasting evidence that evaporation/condensation is also important, as concentrations are enhanced in the smallest particles.

Table 2 Main ICP operating conditions

Parameter	Value
Generator Frequency (MHz)	27.15
Power RF (kW)	1.65
Plasma gas flow rate (l min^{-1})	20.0
Auxiliary gas flow rate (l min^{-1})	0.8
Aerosol carrier gas flow rate (l min^{-1})	0.5
Sample gas flow rate (l min^{-1})	0.125
Injector tube diameter (mm)	1.8
Read time (s)	44
Nebuliser Desolvator Temperature (°C)	170
Nebuliser Condenser Temperature (°C)	0

Table 3 Selected emission lines monitored by ICP-OES

Element	Wavelength (nm)	Element	Wavelength (nm)
Cadmium	214.438	Mercury	194.227
Cadmium	226.502	Mercury	253.652
Cadmium	228.802	Mercury	435.835
Calcium	396.847	Potassium	766.491
Calcium	422.673	Sodium	588.995
Chromium	283.563	Sodium	589.592
Iron	259.941	Tin	242.949
Iron	373.486	Tin	303.412
Lead	261.418	Zinc	202.548
Lead	283.305	Zinc	206.191
Lead	405.778	Zinc	213.856

Table 4 Typical MSW analysis for 7 two hour averaged samples (Morf et al., 2000)

Property	Minimum value	Maximum value	Mean Value	Coefficient of variation (%)
Calorific Value (kj kg^{-1})	8400	12400	10900	15
Ash content (%)	27.7	35.7	32.8	8
Carbon (g kg^{-1})	193	271	234	12
Chlorine (g kg^{-1})	10.4	14.8	13.2	11
Sulphur (g kg^{-1})	4.2	4.6	4.4	4
Cadmium (mg kg^{-1})	7.6	14.7	11.5	20
Copper (mg kg^{-1})	330	950	640	32
Lead (mg kg^{-1})	290	660	430	27
Zinc (mg kg^{-1})	1040	1470	1300	10

Table 5 A comparison of relative metal concentrations found in flue gas by the CEML with concentrations reported in solid residues from incineration (standardised with respect to lead)

Metal	CEML	Particulates <2μ (Greenberg et al., 1978)	MSWI residues from flue gas from (Belevi and Moench, 2000)
As	0	0.0022	0.0024
Ba	0	0.0092	0.13
Ca	0.25	0.24	11*
Cd	0.019	0.011	0.024
Co	0	0.00012	0.0010
Cr	0	0.0051	0.056
Cu	0.15	0.021	0.069
Fe	0.0069	0.0934	1.9
Hg	0.051	0	0.00050
K	14	NA	1.9
Mg	0	0.070	0.53
Mn	0	0.015	0.041
Na	7.3	1.0	2.1
Sb	0.073	0.025	0.092
Sn	0.21	0.11	0.11
Zn	2.1	1.2	2.2

* This figure will be complicated by the addition of lime to the flue gas to capture contaminants

Table 6 System detection limits (mg m^{-3})

Element	Detection Limit (mg m^{-3})
As	0.00271
Ba	0.0174
Ca	0.0589
Cd	0.00623
Co	0.00743
Cr	0.0131
Cu	0.00571
Fe	0.0315
Hg	0.0143
K	0.0765*
Mg	0.0275
Mn	0.0119
Na	0.0438*
Sb	0.00604
Sn	0.0175
Zn	0.0141

* Probably an over-estimate, due to measurable concentrations of the analyte in the assumed "blank" signal

Figure 1 Schematic diagram of the waste incinerator plant, showing the sampling location

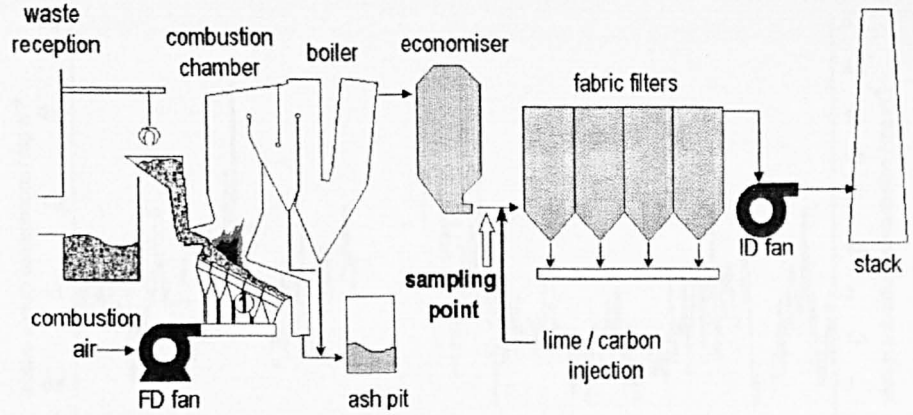


Figure 2 Sodium concentrations for a 4.5 Hour Period as measured on the 589.592 nm emission line (NB Gaps in this and subsequent emission measurements are due to cleaning of the sample probe and cyclone to remove deposited ash).

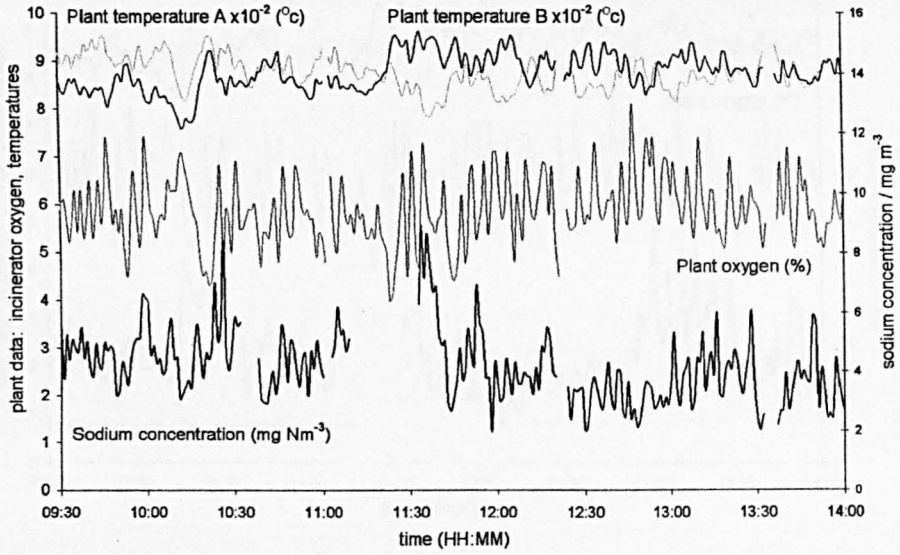


Figure 3 Comparison of sodium and potassium concentrations for a 4.5 hour period, showing high correlation, but not exact overlay

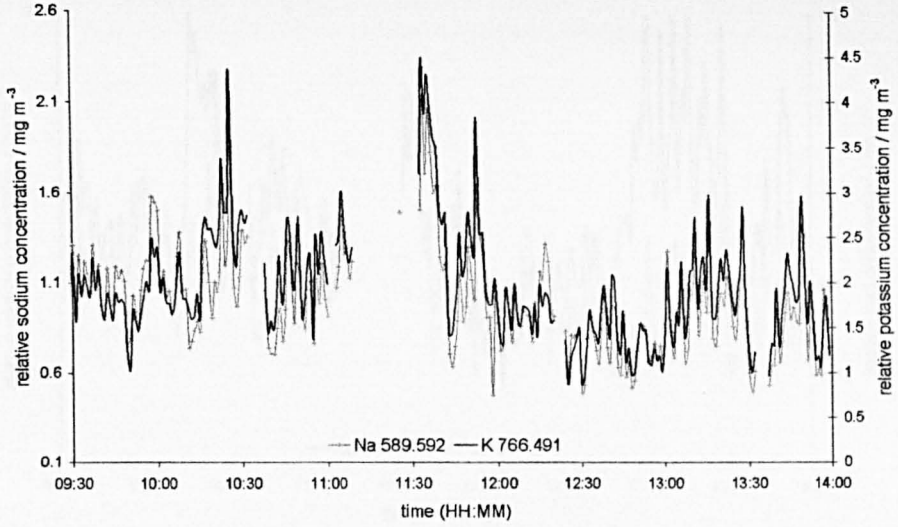


Figure 4 Lead concentrations for a 4.5 hour period as measured on the 405.778 nm emission line

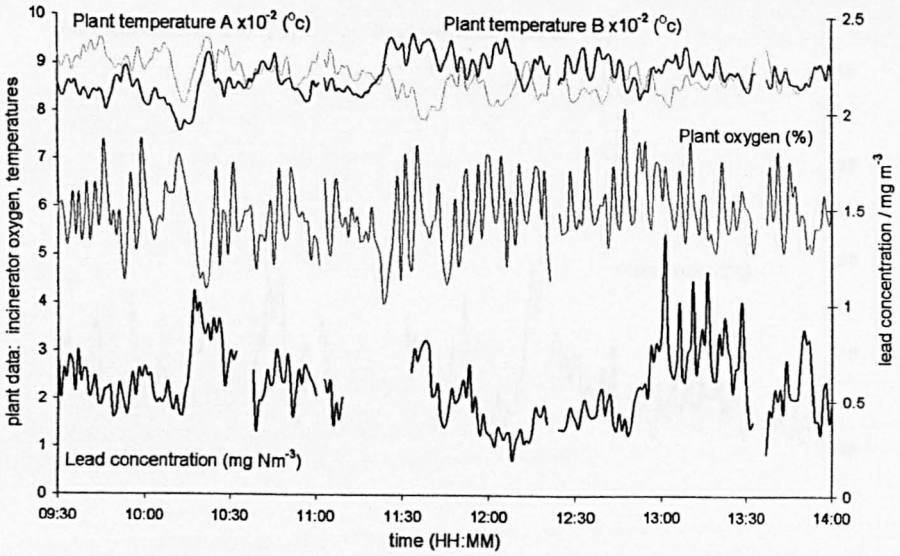


Figure 5 Comparison of sodium and lead concentrations for a 4.5 hour period, showing some (incomplete) correlation.

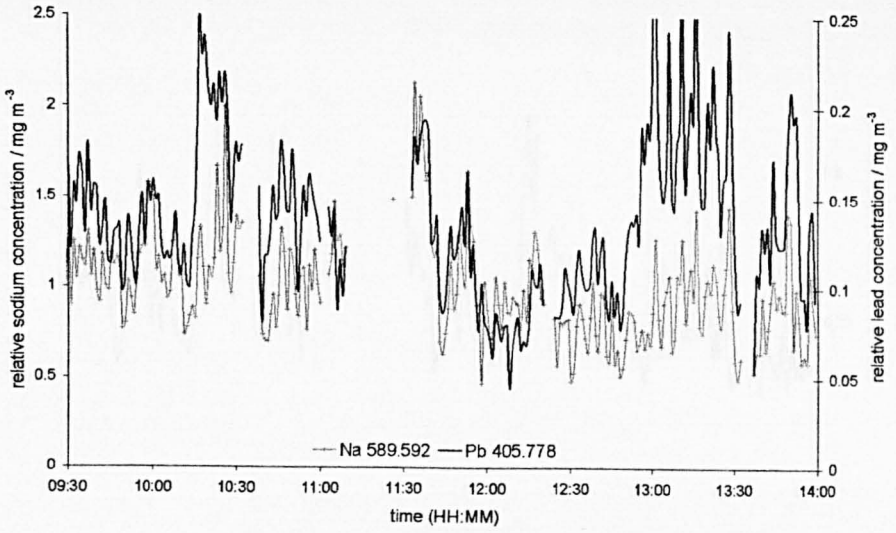


Figure 6 Zinc concentrations for a 4.5 hour period measured on the 213.856 nm line

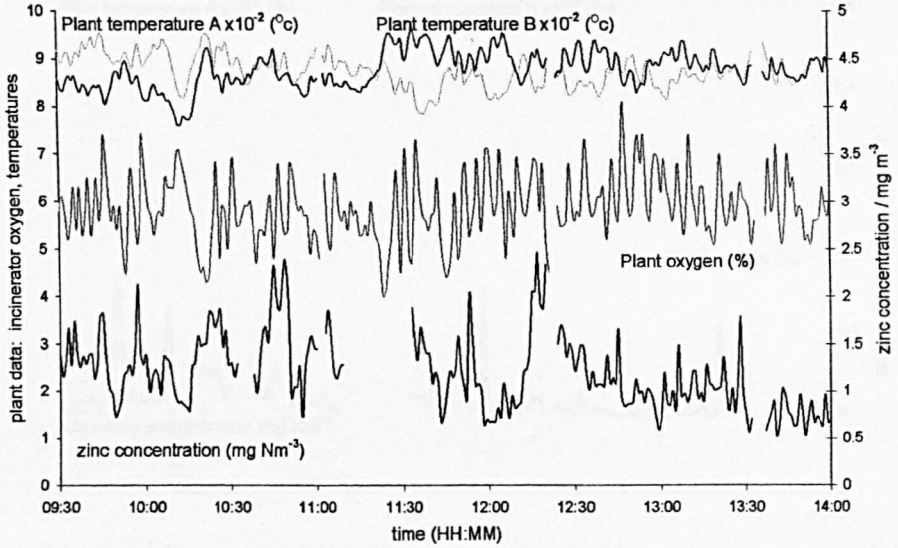


Figure 7 Comparison of sodium and zinc concentrations for a 4.5 hour period, showing some (incomplete) correlation.

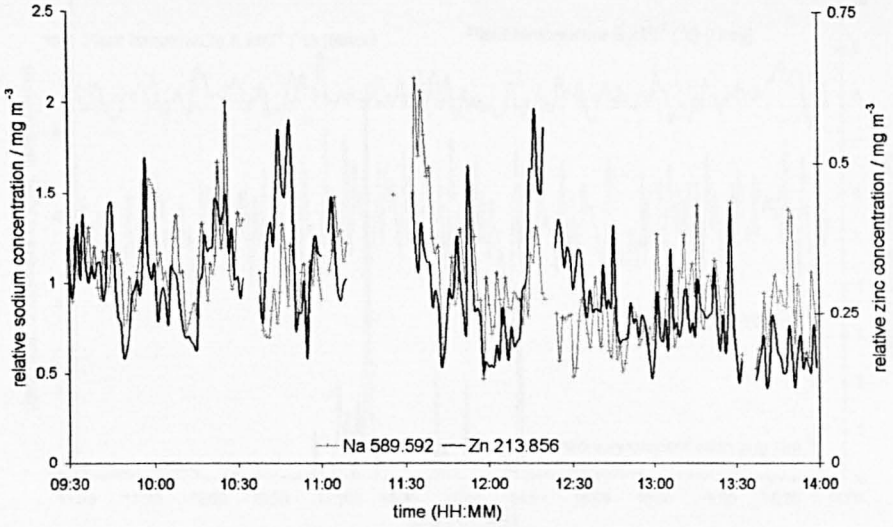


Figure 8 Cadmium concentrations for a 4.5 hour period as measured on the 226.503 nm wavelength

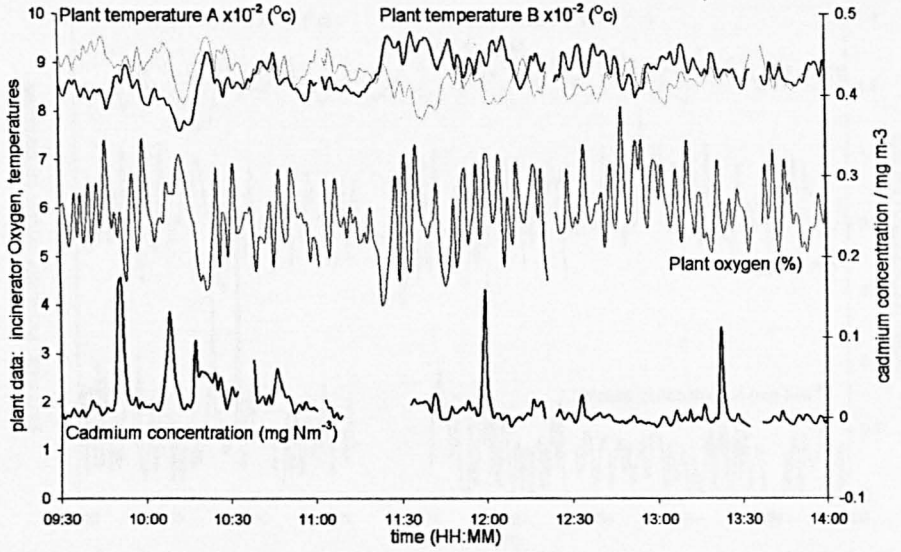


Figure 9 Mercury concentrations for a 6 hour period as measured on the 253.653 nm wavelength

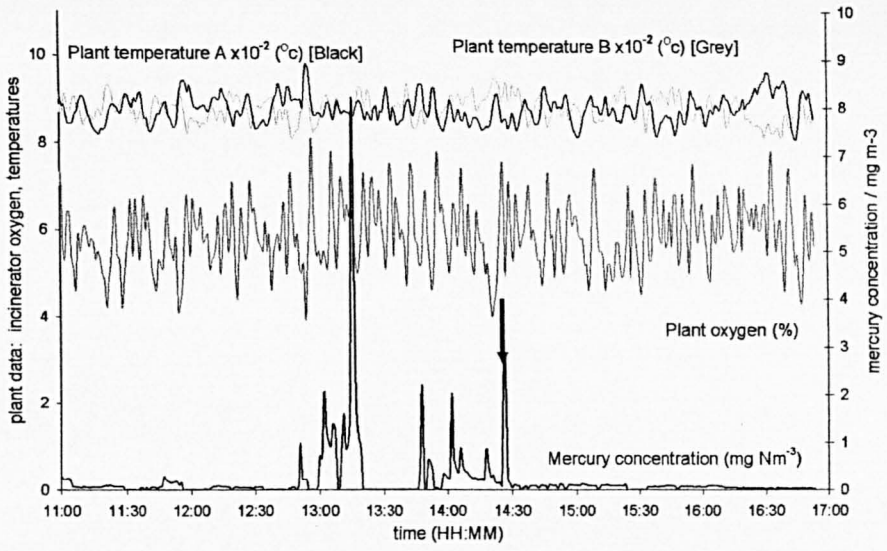
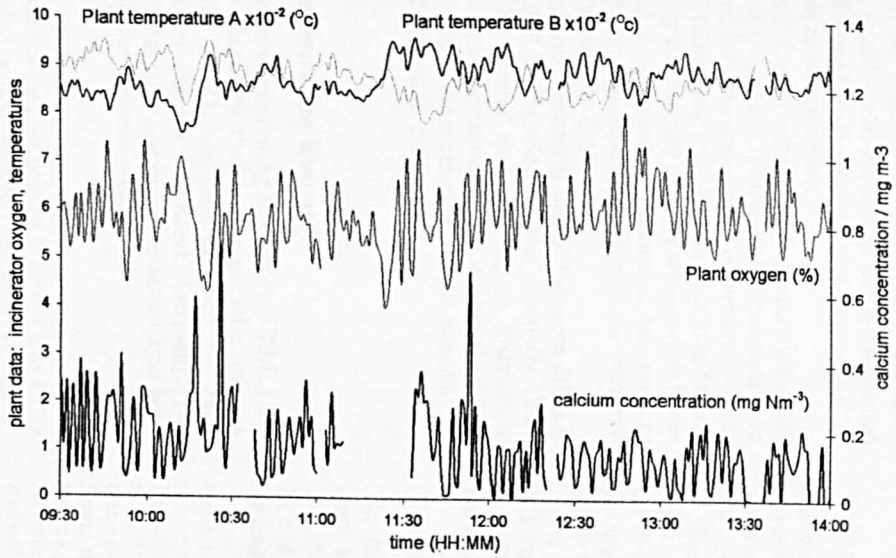


Figure 10 Calcium concentrations for a 4.5 hour period as measured on the 422.673 nm wavelength



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Continuous measurement of mercury in flue gas using ICP-OES†

P. J. Clarkson,*[a] D. J. Poole,[a] V. N. Sharifi,[a] J. Swithenbank,[a] H.-J. Waarlo,[b] D. Ardelt[b] and H. Falk[b]

[a]*Sheffield University Waste Incineration Centre, Department of Chemical and Process Engineering, Mappin Street, Sheffield S1 3JD. E-mail: p.j.clarkson@sheffield.ac.uk; Fax: +44 (0)114 222 7501; Tel: +44 (0)114 222 7570*
[b]*SPECTRO Analytical Instruments GmbH, Boschstr. 10, 47533 Kleve, Germany*

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A system capable of continuously measuring mercury using ICP-OES, in the effluent gases from incineration and other industrial processes, has been verified using an experimental furnace.

Introduction

Experimental continuous emissions monitoring (CEM) techniques began appearing in the literature in the mid-1990s.[1,2] The techniques described in the literature are inductively coupled plasma-mass spectrometry,[3] laser induced plasma spectrometry,[4] microwave-induced plasma spectroscopy,[5] air inductively coupled plasma optical emission spectroscopy,[6] and also argon inductively coupled plasma-optical/atomic emission spectrometry.[7]

One of the major challenges for CEM techniques has been obtaining accurate gas-phase calibrations.[8,9] Due to potential losses in the gas sampling system, it has been questioned whether laboratory based calculations are representative of samples introduced at the start of the sample collection system.[10] This experiment describes the practical verification of a laboratory calibration, using a volatile metal introduced into a combustion system, thereby confirming both the laboratory calibration and the efficacy of the sample collection system.

Mercury was chosen for this experiment as mercury is volatile, having a high vapour pressure at relatively low temperature. In addition, it undergoes few interactions with incinerator or other combustion systems, minimising complications due to in-furnace reactions.[11,12] Mercury and mercury chloride are known to be the major species found in large-scale combustors, but mercury chloride was avoided for this experiment, due to the increased chances of interaction with the system.[11]

It should be noted that mercury is one of the more difficult metals to detect by ICP, having relatively low sensitivity. Thus, it may reasonably be inferred that if it can be successfully measured at gas-phase concentrations approaching the calculated detection limit other, more sensitive, metals may also be detected, if they are present in the flue gas.

Experimental

Continuous emissions monitoring laboratory

The continuous emissions monitoring laboratory (CEML) is a self-contained mini-laboratory that is transportable using a crane and lorry. The CEML has been designed and built by project collaborator Spectro AI, Kleve, Germany. The specifications of the laboratory and instrumentation have been described in detail in our previous paper.[13]

Instrumentation

All determinations were carried out using a Spectro Ciros-CCD ICP-OES with radial view configuration (Spectro AI, Kleve, Germany). The torch used for the analysis was a custom-built demountable torch with an injector id of 1.8 mm, to allow for the higher flow of coolant gas and higher power needed to sustain the plasma under atmospheric conditions.

Data was collected using the Spectro Smart Analyser software. A signal integration time was set at 24 s. General operating parameters are shown in Table 1.

Samples and sample collection

The sampling system is often the weakest part of a continuous monitoring system for gaseous samples, and the following design is based upon the experience of those most experienced in gas analysis system design.[14] A 40 m heated sampling line (PTFE lined, id = 12 mm) was used to isokinetically sample gas from the flue of the test furnace at gas flow rates of 60 L min^{-1}. The sample line was operated at a temperature of 200 °C, to minimise deposition, and avoid problems of condensation. A continuous low flow rate sub-sample was taken, using a double head, out of phase, peristaltic pump *via* a secondary sampling stage at 0.24 L min^{-1}.

Calibration

Calibration was achieved by introducing a standard aerosol, prepared *in situ* using a modified lichte nebuliser. The nebuliser conditions were: peristaltic pump speed = 2, nebuliser gas flow 0.8 L min^{-1}, additional flow 0.7 L min^{-1}.

Elemental calibration standards were prepared from a stock solution (BDH, Poole, Dorset) covering the range 0.0104 mg m^{-3} to 2.082 mg m^{-3}, the nebuliser efficiency having been previously determined by means of a mass-balance. Elemental calibrations were made with additional argon flow being used to maintain the total gas through the ICP torch at the level usually encountered when gas samples were being taken. Mercury was measured at 253.652 nm, with background corrections being made instrumentally.

The test furnace

The test furnace used was a small, fixed bed device, made of steel, and refractory lined. It was heated with an electrically controlled gas oil burner, capable of operating at between 28 and 60 kW of thermal output, with current burner settings leading to a thermal output of 30–32 kW. The exhaust gases

Table 1 ICP operating parameters

Parameter	Value
Generator frequency/MHz	27.15
Power rf/kW	1.7
Plasma gas flow rate/l min^{-1}	20.0
Auxiliary gas flow rate/l min^{-1}	0.8
Aerosol carrier gas flow rate/l min^{-1}	0.8
Sample gas flow rate/l min^{-1}	0.24
Injector tube diameter/mm	1.8
Stabilisation time/s	15
Read time/s	40

† Electronic supplementary information (ESI) available: the emission profile for mercury. See http://www.rsc.org/suppdata/ja/b4/b400578c/

DOI: 10.1039/b400578c

generated passed through a vertical chimney and were released to the atmosphere without any gas clean-up. Gases were sampled by the CEML from a sampling point in the chimney, about 40 cm below the top. The furnace was fitted with a side entry port, to allow the introduction of solid samples directly into the combustion chamber, on a stainless steel probe.

Metal spikings in the test furnace

Small spikes of elemental mercury (99.99%, Sigma–Aldrich, Gillingham, Dorset) were added to the stainless steel sample introduction probe, which was placed in the furnace to allow evaporation. Sample masses between 0.0015 and 0.0258 g were added. The practicalities of the experimental system prevented smaller samples being introduced to the furnace as they could not be weighed accurately, so all spikings were above anticipated detection limits.

The concentration of metal present in the flue gas of the furnace was measured throughout the experiment using the ICP. The measured gas-phase concentrations were used to calculate the total amount of metal accounted for in the flue gas, and the mass of metal added was compared with the output.

Results and discussion

Continuous measurements

The emission profile for mercury observed in the flue gas of the furnace during the metal spiking experiment is shown in Fig. S1†. Twelve emission events are clearly observed, corresponding to twelve spiking events, two of which have been excluded from calculations as outliers. The maximum concentrations on the profile are approximately 8 mg m^{-3}, for a furnace spike of 25 mg of mercury.

It should be noted that the responses do not appear to be significantly altered by changes in carbon dioxide emission or other interferences, and that as such observed variations in signal response do correspond to changes in flue metal concentration. Good baseline resolution is observed between emission events.

Calculation of total mercury in flue gas based on measured concentration

A spiking event in the furnace results in a spike of mercury in the flue gas of up to 8 mg^{-3}, and typically lasting 3–4 min. A measurement of mercury in the flue gas was recorded every 26–27s. As the total flow of gas through the test furnace was known, the total amount of mercury released in the flue gas during a single measurement event could be calculated.

A comparison of the amounts of mercury added to the furnace with the calculated amount released from the furnace flue is shown in Fig. 1 ($y = 1.0296x - 1.2398$, $r^2 = 0.9677$). Agreement between the measured and calculated values is generally very good.

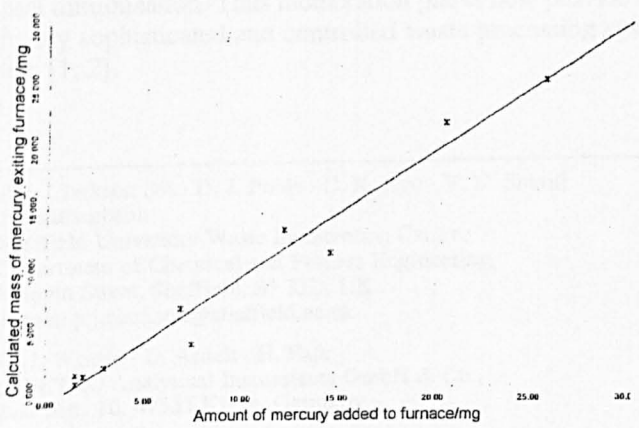

Fig. 1 A comparison of mercury additions to the test furnace with calculated mercury emissions from the furnace.

Conclusion

From the data presented in this work it has been shown that it is possible to quantitatively measure emission concentrations for elements in the gas phase using ICP-OES. This experiment has confirmed that the use of a nebuliser to generate an aqueous aerosol of standard is an acceptable method of calibration of a gas-phase measurement system. While the significance of the effect of changing gas composition (water, oxygen and carbon dioxide concentrations) makes quantitative measurement challenging, this experiment has demonstrated that a good correlation is achieved between measurements of gas phase metal and known metallic input in laboratory conditions.

The authors believe that the verification method used in this experimental programme is the best possible method for ensuring the satisfactory behaviour of the whole analytical system, as it emulates as nearly as possible the type of matrix and variability observed in an industrial combustion system. It is believed that the outliers observed are due to the experimental technique, where a small quantity of mercury is being distributed into a large volume of gas, rather than the performance of the analytical system itself. The analysis has been proven to be both sensitive and accurate in a difficult analytical situation.[13]

Although agreement is generally good between measured and calculated values, some outliers have been observed. In two cases, the measured amount of metal was slightly higher than the added amount. This could be due to a memory effect of mercury in the furnace or analytical system, or could be as a result of the assumptions made in the experimental design.

The data presented here show that the system may be successfully calibrated using aqueous standards to accurately measure metals in flue gases. This is a significant advance towards the acceptance of the accuracy of a developing continuous monitoring technology for metals in gaseous samples.

In continuing the development of the CEML system, and building on the work carried out to date, investigation will continue into the stability of the analytical system in a gas which has significantly variable bulk composition. In addition, investigations will be conducted into the measurement of metals which are volatile enough to be released into the gas phase, but which re-condense early in the combustion system, so require measurement as an aerosol of solid particles.

Acknowledgements

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SPECIAL ISSUE PAPER

P. J. Clarkson · D. J. Poole · C. K. Ryu · V. N. Sharifi
J. Swithenbank · H.-J. Waarlo · D. Ardelt · H. Falk

Continuous measurement of metals in flue gas using ICP-OES

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Abstract A system capable of continuously measuring a range of metallic elements in the effluent gas from incinerators and other similar industrial processes, and providing on-line results has been developed. With a state-of-the-art mobile laboratory measurements were taken from a UK municipal solid waste incinerator. The detection system used was an ICP-OES, with a modified torch to allow the introduction of flue gas directly into the plasma. Metals that were investigated were Ni, Hg, V, Al, Na, Ca, Cu, Sn, Pb, Sb, As, Cd and Tl, with limits of detection in the range 0.0004 mg m^{-3} to 0.1 mg m^{-3} being calculated. Emission measurements produced data that showed that the MSWI plants emission were significantly lower than the emission limits specified in EC 2000/76/EC.

Keywords Flue gas · Continuous emission monitoring · ICP-OES · Metals · On-line analysis

Introduction

Incineration is often seen as an undesirable and environmentally unacceptable form of waste management. Much of the opposition appears to be based on the historic reality of incinerators, which were poorly controlled and highly polluting. Much is now known about the combustion process, formation of pollutants and pollutant removal or impact minimisation. Thus incineration plants now provide a highly sophisticated and controlled waste processing system [1, 2].

P. J. Clarkson (✉) · D. J. Poole · C. K. Ryu · V. N. Sharifi
J. Swithenbank
Sheffield University Waste Incineration Centre,
Department of Chemical and Process Engineering,
Mappin Street, Sheffield, S1 3JD, UK
e-mail: p.j.clarkson@sheffield.ac.uk

H.-J. Waarlo · D. Ardelt · H. Falk
SPECTRO Analytical Instruments GmbH & Co.,
Boschstr. 10, 47533 Kleve, Germany

At present between 5% and 9% of UK controlled waste is incinerated, and as energy can be recovered from incinerated material, through electricity generation, or district heating schemes, in this context, waste is seen as a renewable energy source, and so contributes to the electricity generation non-fossil fuel obligation (NFFO). Incinerator operating conditions are tightly controlled, so if operating within legislative limits, incineration is a relatively clean process for the disposal of waste, where none of the available options are ideal [3].

Current EC legislation limits permissible pollutant levels in gases, liquids, and solids resulting from incineration. These regulations require the continuous measurement of bulk pollutant constituents, such as SO_2, HCl and dust, and extractive sampling of trace metal and organic pollutants [4].

Traditional extractive monitoring methodologies require the taking of discreet samples with subsequent laboratory based analysis. The development of real-time monitoring of element and heavy metals in gaseous samples is, therefore, seen as a major breakthrough in both the understanding of industrial processes and in the measurement of emissions for legislative purposes.

Without continuous and cost-effective sampling and analysis programmes, proper understanding of the elemental emissions from combustion processes will not be realised and hence, it will not be possible to develop informed control strategies designed to minimise gaseous emissions of toxic-metals. Current emissions legislation indicates that it is the intention of regulatory bodies to introduce continuous monitoring of metals, as soon as adequate technology becomes available [4, 5].

Experimental continuous emissions monitoring (CEM) techniques began appearing in the literature in the mid-1990s [6, 7]. Previously, there had been very little by way of multi-element continuous monitoring which may have been applicable to gaseous emissions from industrial processes. The techniques described in the literature are inductively coupled plasma – mass spectrometry [8], laser induced plasma spectrometry [9] (also known as spark-induced breakdown spectroscopy), microwave-induced plasma

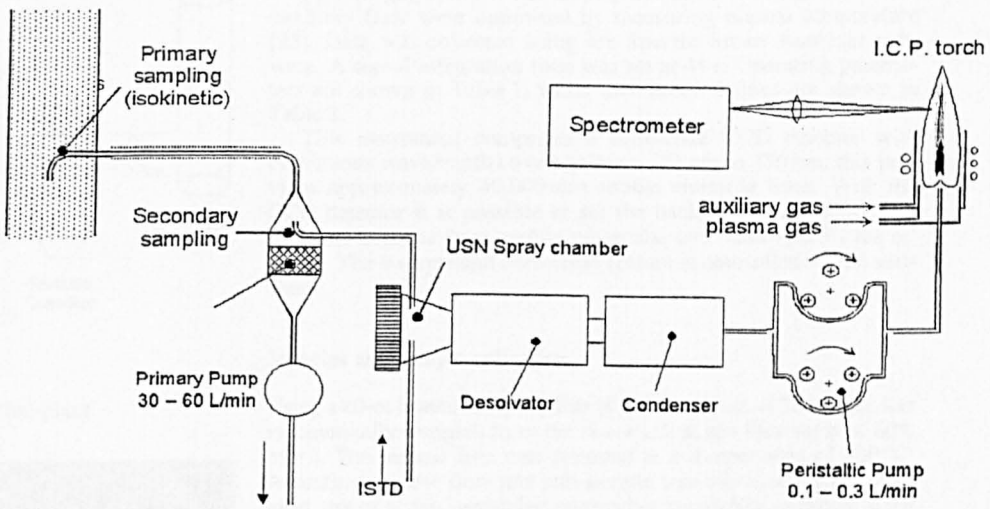


Fig. 1 Schematic diagram of the CEM-ICP-OES system

spectroscopy [10], air inductively coupled plasma optical emission spectroscopy [11, 12, 13], and also argon inductively coupled plasma – optical/atomic emission spectrometry [14, 15, 16]. However to date, despite significant advances in these techniques, all of which are plasma based, none have been found to meet the quality requirements for regulatory endorsement [17, 18, 19]. Recent developments have either been in the laser- or microwave-induced plasma techniques [18, 20], or in argon-ICP-OES [16, 21]. Meyer and Seltzer continue to work on an argon-ICP-OES system, but this is significantly different from the technique described here, in that the gas sampling system is different. Their technique uses a recirculating sample loop, analogous to the sample loop on an HPLC, whereas our system relies on a continuous subsampling from the isokinetic sample drawn from the flue [22].

The work presented here focuses on the measurement of the metals, that are required by current legislation, in the gaseous emission from an municipal solid waste incinerator. Data was obtained using a state-of-the-art mobile laboratory-based continuous emission monitoring system using ICP-OES-CCD detection. This unique system, built in collaboration with Spectro AI, is a self-contained laboratory that is designed to be used at industrial locations for the measurement of gaseous emissions.

Experimental

Continuous emission monitoring laboratory

The continuous emission monitoring laboratory (CEML) is a self-contained mini laboratory that is transportable using a crane and lorry. The CEML has been designed and built by project collaborator Spectro AI, Kleve, Germany. The dimensions of the CEML are 6.5 m×2.4 m with an overall height of 3.5 m, and a nominal weight of 7.2 tonnes.

The CEML requires a mains power supply of 30–40 kVA and supplied through an externally mounted 40 kKA transformer. The CEML also is supplied with an externally mounted 230-L capacity cryotank, for liquid argon.

Table 1 ICP operating parameters

Parameter	Value
Generator Frequency (MHz)	27.15
Power RF (kW)	1.7
Plasma gas flow rate (L min^{-1})	20.0
Auxiliary gas flow rate (L min^{-1})	0.8
Aerosol carrier gas flow rate (L min^{-1})	0.7
Sample gas flow rate (L min^{-1})	0.24
Injector tube diameter (mm)	1.8
Stabilisation time (s)	15
Read time (s)	40

Table 2 Element emission lines

Element	Wavelength (nm)
Carbon (I)	247.856
Nitrogen (I)	174.273
Oxygen (I)	130.485
Argon (I)	430.010
Sodium (I)	589.592
Calcium (II)	393.366
Aluminium (I)	396.152
Thallium (I)	276.800
Tin (I)	303.413
Lead (II)	405.785
Antimony (I)	252.852
Arsenic (I)	193.759
Nickel (I)	341.476
Copper (I)	324.754
Cadmium (II)	226.502
Mercury (I)	253.652

Instrumentation

All determinations were carried out using a Spectro Ciros-CCD ICP-OES with radial view configuration (Spectro AI, Kleve, Germany). The torch used for the analysis was a custom built demountable torch with an injector i.d. of 1.8 mm, to allow for the higher flow of coolant gas and higher power, needed to sustain the plasma under atmospheric conditions. Fig. 1 shows a schematic diagram of the instrumental configuration.

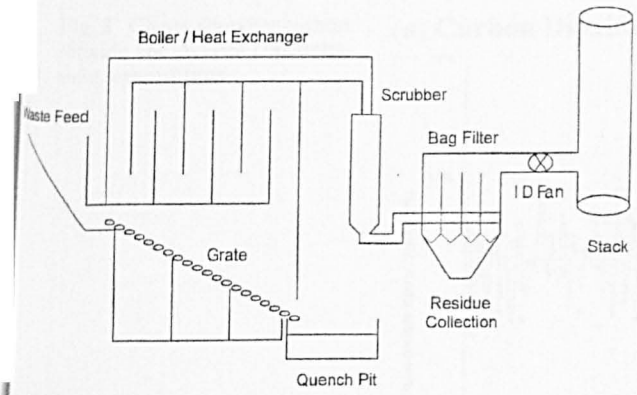


Fig. 2 Schematic diagram of the incineration plant

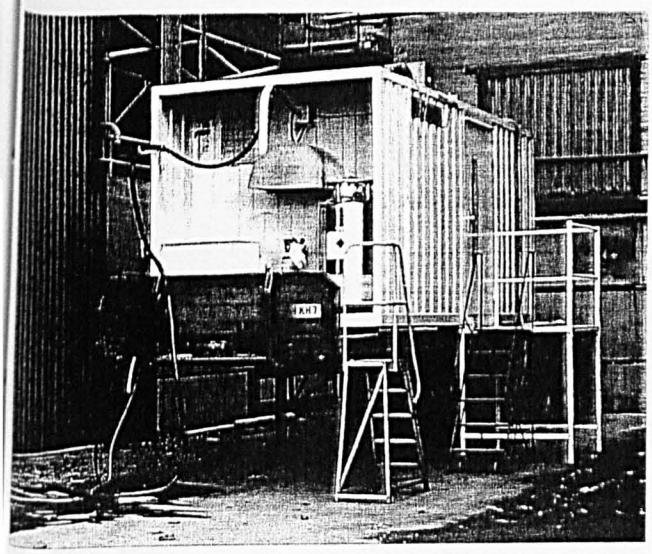


Fig. 3 Image of continuous emissions monitoring laboratory at MSWI plant

Plasma gas flows, such as coolant flow, nebuliser flow and auxiliary flow were optimised by measuring plasma temperature [23]. Data was collected using the Spectro Smart Analyser software. A signal integration time was set at 44 s. Operating parameters are shown in Table 1, while the emission lines are shown in Table 2.

This instrument comprises a solid-state CCD detector with continuous wavelength coverage from 125 nm to 770 nm, this provides approximately 40,000 measurable emission lines. With the CCD detector it is possible to set the background corrections so that interferences from carbon molecular and other species are reduced. The background correction feature is controlled by the software.

Samples and sample collection

Using a 40-m heated sampling line (PTFE lined, i.d.=12 mm) gas was isokinetically sampled from the flue stack at gas flow rates of 60 L min^{-1}. The sample line was operated at a temperature of 200 °C. A continuous low flow rate sub-sample was taken, using a double head, out of phase, peristaltic pump via a secondary sampling stage at 0.24 L min^{-1}.

Calibration

Calibration was achieved by introducing a standard aerosol, prepared in-situ using a Spectro USN200 Ultrasonic Nebuliser (USN) with the carrier gas being drawn through the USN by the peristaltic pump. The ultrasonic nebuliser conditions were: heater temperature 160 °C, cooler temperature 2 °C with a carrier gas flow being 0.24 L min^{-1}. The USN is used to provide a dry aerosol that contains the elements of interest, as well as to normalise the water content of the sample gas, thus making the calibration conditions as close to the sampling conditions as possible.

Elemental calibration standards were prepared from a stock solution (BDH, Poole, Dorset) covering the range 1.2 ng m^{-3} to 0.12 mg m^{-3}. Elemental calibration measurements were taken at different carbon dioxide concentrations. Artificial flue gas mixtures were prepared with carbon dioxide concentrations of 0%, 5% and 10%. These mixtures were prepared from nitrogen, oxygen and carbon dioxide cylinders through suitable mass flow controllers. Carbon dioxide calibration is also measured using these

Fig. 4 Chart showing relationship between carbon emission signal and carbon dioxide concentration

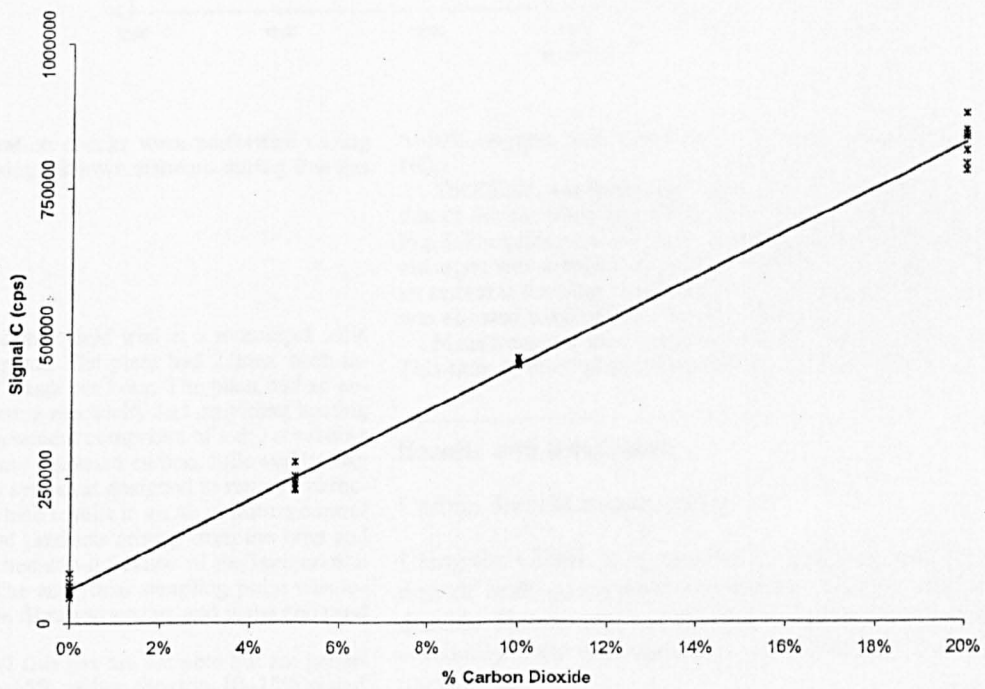
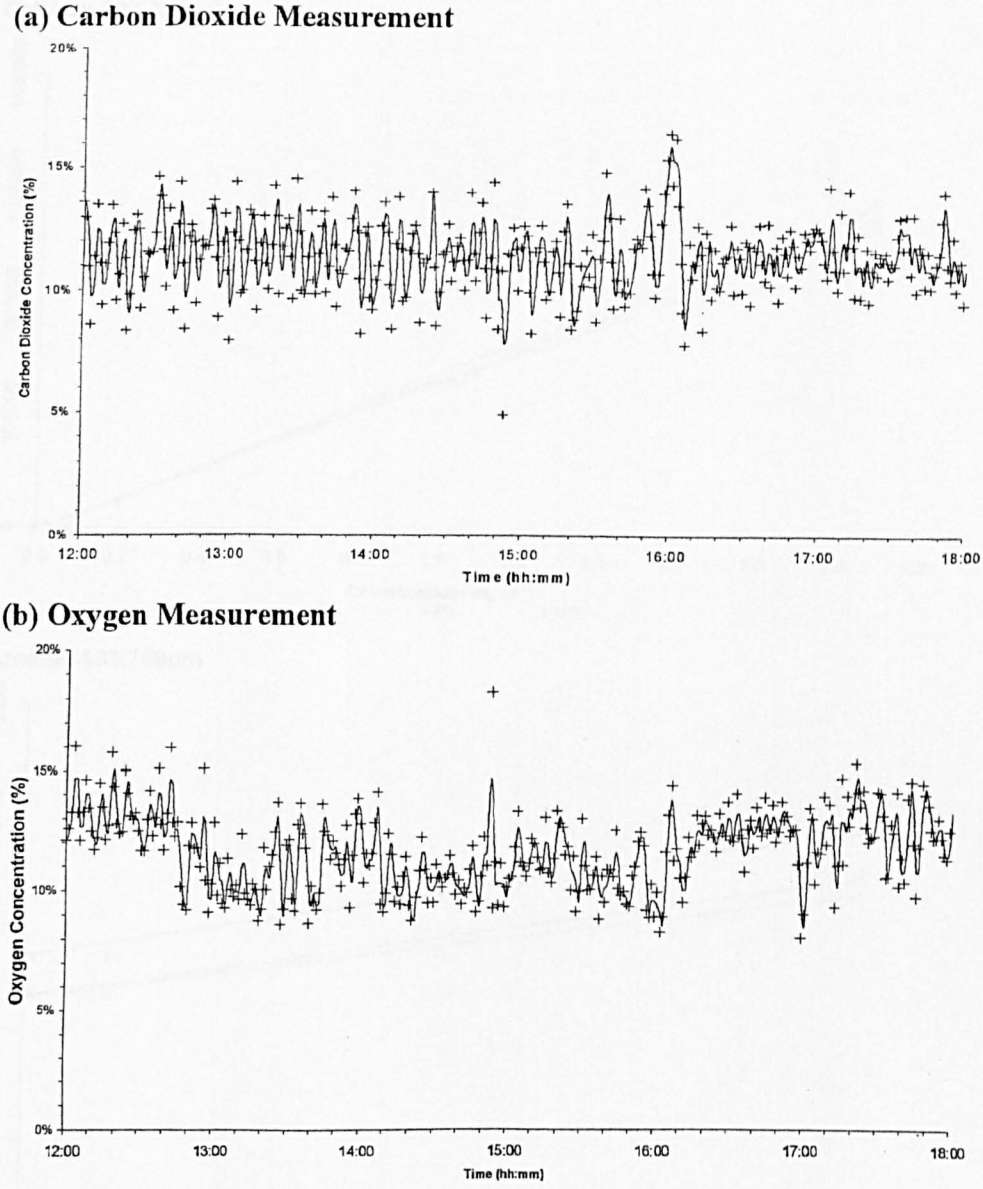


Fig. 5 Charts showing carbon dioxide and oxygen concentrations against time



gas mixtures. On-line calibration checks were performed during experimental runs by nebulising a known standard during flue gas measurements.

Industrial plant studies

The CEML system was used in a field trial at a municipal solid waste incineration (MSWI) plant. The plant had 2 lines, each incinerating up to 12 tonnes of waste per hour. The plant had an energy recovery system, generating electricity and providing heating to local buildings. Flue gas treatment comprised of a dry scrubbing system using hydrated lime and activated carbon, followed by bag filters. The plant gas cleanup system is designed to remove particulate matter down to 5 μm, which results in an air pollution control residue containing fly ash and products arising from the lime and carbon cleanup system. A schematic overview of the incineration process is shown in Fig. 2. The analytical sampling point was located in the duct following the filtration system and is the one used for legislative sampling.

The constituents of MSWI flue gas are variable but are generally considered to contain 10–15% carbon dioxide, 10–15% water, 5–10% oxygen, with trace levels of carbon monoxide, SO_x and NO_x.

The CEML was transported to the plant by lorry and for the duration of the sampling regime was left on the trailer. This is seen in Fig. 3. The plant provided power and water to the CEML, and the liquid argon was supplied on-site by Cryoservice (Worcester, UK). After arrival at the plant, the CEML was powered up and the ICP-OES was allowed to equilibrate for 24 h before use.

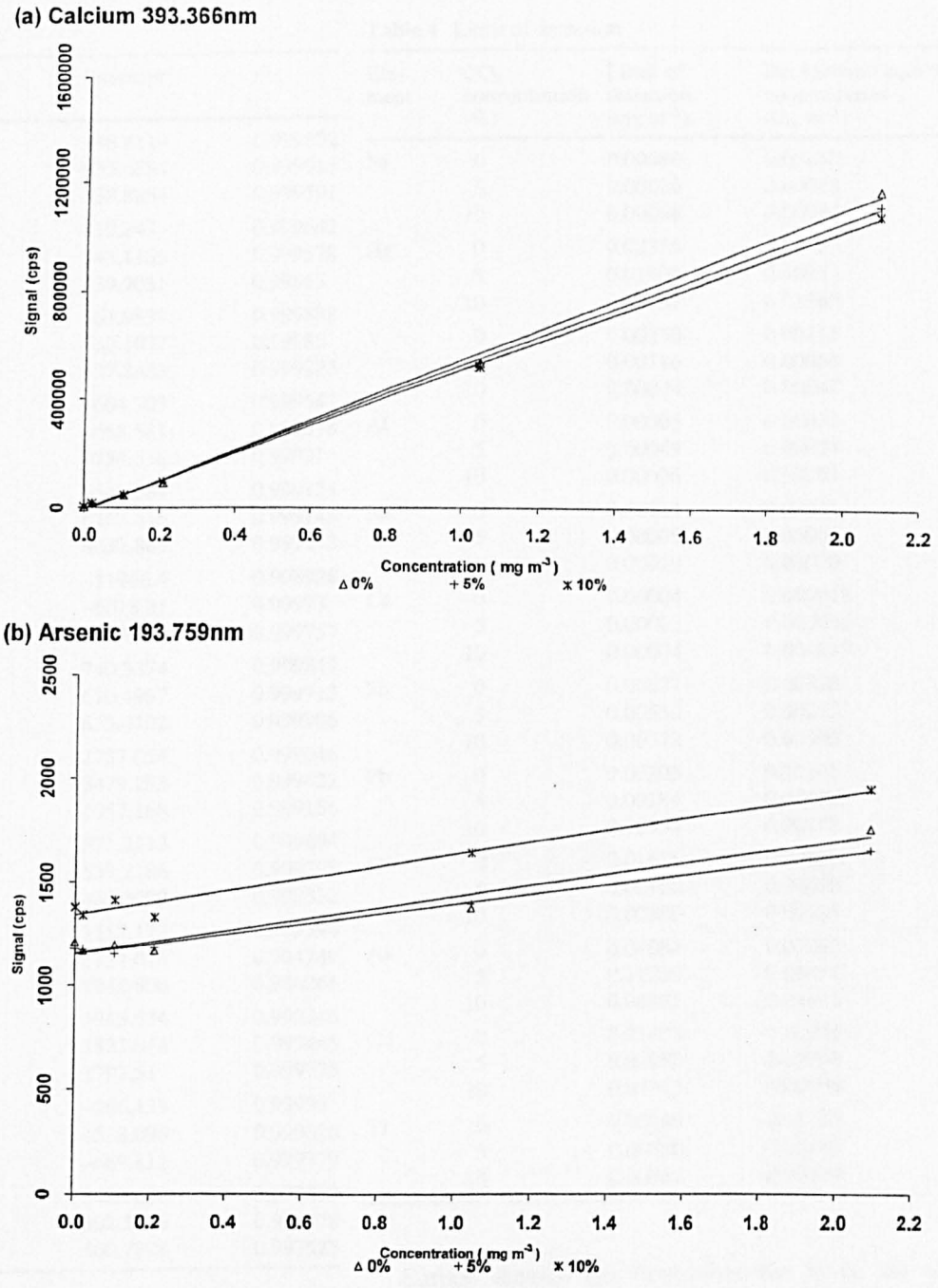
Measurements were taken over an extended sampling period. This time covered plant waste delivery and shift change overs.

Results and discussion

Carbon dioxide measurement

Using the CEML it is possible to measure the concentration of bulk gases such as oxygen, nitrogen and carbon dioxide. However at a municipal solid waste incinerator, it is usually only necessary to measure oxygen and carbon monoxide.

Fig. 6 Calibration curve for calcium and arsenic



Using artificial flue gas of known concentrations, emission signals were measured at 130.485 nm for oxygen, 247.856 nm for carbon and 430.010 nm for argon. Figure 4 shows the plot of carbon emission signal and carbon dioxide concentration. From this it is possible to see that there is a linear relationship between carbon signal and carbon concentration. A similar relationship is also seen between oxygen concentration and the oxygen emission signal.

As oxygen and carbon signals are linked it is possible prepare a calibration plot by plotting carbon (or oxygen) concentration verses corrected signal. The corrected signal is calculated from Eq. 1. To calculate oxygen concentration, the carbon and oxygen emission signals are inverted in the equation.

$$Sig_{corr} = \frac{C_{sig}}{O_{sig}} \times Ar_{sig} \quad (1)$$

It is therefore possible to calculate the slope and intercept for this slope, from which it is possible to calculate the concentration in an analytical sample.

As part of an industrial trial that will be discussed in a later section, bulk gas composition was measured. The carbon dioxide and oxygen concentrations are shown in Fig. 5, where it is observed that in general there is an inverse correlation between oxygen and carbon dioxide.

In order to assess the validity of the data obtained from the CEML it was necessary to obtain data from an alternative source. During the trials, carbon dioxide and oxy-

Table 3 Calibration statistics

Element		Slope	Intercept	r^2
Ni	0%	45308.37	948.6119	0.999892
	5%	44706.02	935.6884	0.999913
	10%	44053.07	838.8854	0.999591
Hg	0%	922.8003	410.247	0.999642
	5%	906.2942	343.1156	0.999578
	10%	874.4452	339.9031	0.99865
V	0%	21660.2	661.9839	0.999838
	5%	21542.28	580.1077	0.99985
	10%	21534.93	427.2433	0.999225
Al	0%	53906.57	–604.703	0.999547
	5%	54419.32	–668.581	0.999578
	10%	54741.61	–754.536	0.99921
Na	0%	249819.7	6540.084	0.999739
	5%	240418.3	6267.646	0.999149
	10%	244756.5	8037.863	0.997173
Ca	0%	559802.9	–11966.4	0.998928
	5%	534351.9	–6018.21	0.99973
	10%	517055.9	–5699.88	0.999757
Sn	0%	3445.364	740.3374	0.999849
	5%	3368.34	610.4997	0.999713
	10%	3264.343	623.4102	0.999786
Pb	0%	7396.693	2737.054	0.999046
	5%	7137.311	3479.283	0.999422
	10%	7045.092	4957.168	0.999156
Sb	0%	1635.286	571.2113	0.999694
	5%	1622.771	539.2186	0.999798
	10%	1608.765	489.3098	0.999332
As	0%	272.3416	1157.173	0.979594
	5%	238.2767	1154.074	0.994749
	10%	290.9608	1342.806	0.986261
Cd	0%	1427.578	1943.534	0.999346
	5%	1408.996	1821.046	0.999465
	10%	1423.485	1797.51	0.999775
Cu	0%	128785.8	–266.439	0.99995
	5%	127972.8	–538.096	0.999896
	10%	125494.3	–669.812	0.999779
Tl	0%	677.3083	342.0636	0.997859
	5%	729.3378	302.5626	0.995878
	10%	706.9044	300.7998	0.997523

Table 4 Limit of detection

Element	CO_2 concentration (%)	Limit of detection (mg m^{-3})	Background equivalent concentration (mg m^{-3})
Ni	0	0.00080	0.00040
	5	0.00026	0.00013
	10	0.00068	0.00034
Hg	0	0.02335	0.01167
	5	0.01905	0.00953
	10	0.02759	0.01380
V	0	0.00230	0.00115
	5	0.00116	0.00058
	10	0.00094	0.00047
Al	0	0.00005	0.00002
	5	0.00049	0.00024
	10	0.00006	0.00003
Na	0	0.00022	0.00011
	5	0.00005	0.00002
	10	0.00019	0.00010
Ca	0	0.00004	0.000018
	5	0.00003	0.000015
	10	0.00004	0.000019
Sn	0	0.00621	0.00310
	5	0.00550	0.00275
	10	0.00772	0.00386
Pb	0	0.00203	0.00101
	5	0.00184	0.00092
	10	0.00554	0.00277
Sb	0	0.01616	0.00808
	5	0.00920	0.00460
	10	0.00389	0.00195
As	0	0.04084	0.02042
	5	0.11229	0.05614
	10	0.08801	0.04401
Cd	0	0.01851	0.00925
	5	0.01937	0.00968
	10	0.01913	0.00956
Tl	0	0.02369	0.01185
	5	0.00530	0.00265
	10	0.00947	0.00474

gen were monitored using gas analysers. Visual observation confirmed that the observed data and calculated data correlated to some degree.

It was also possible to obtain data from the oxygen analysers on the plant and it observed that there is good correlation between the two data sets. However, it should be noted that the location of the oxygen gas analyser was different to the CEML sampling point, and also that the time base of the analyser was different to from that of the CEML system.

The fluctuation in the carbon dioxide content of the gas sample is directly related to the temperature of the furnace. When the temperature drops, and waste is added, highly combustible material will burn rapidly, causing a peak in the carbon content of the flue gas.

Carbon dioxide has been observed to be the major component of the flue gas that affects the plasma. Other combustion by-products such as SO_2 and NO_x are effectively removed from the gas stream by the MSWI plants flue gas treatment system.

Calibration

Calibration curves for calcium and arsenic are shown in Fig. 6. It can be seen that in general, linearity has been obtained over a wide calibration range. The carbon dioxide content of the sample can be seen to affect the calibration, both in terms of sensitivity, as shown by a change in line gradient, and background noise, as shown by intercept value. Calibration details for the full range of elements being discussed are shown in Table 3.

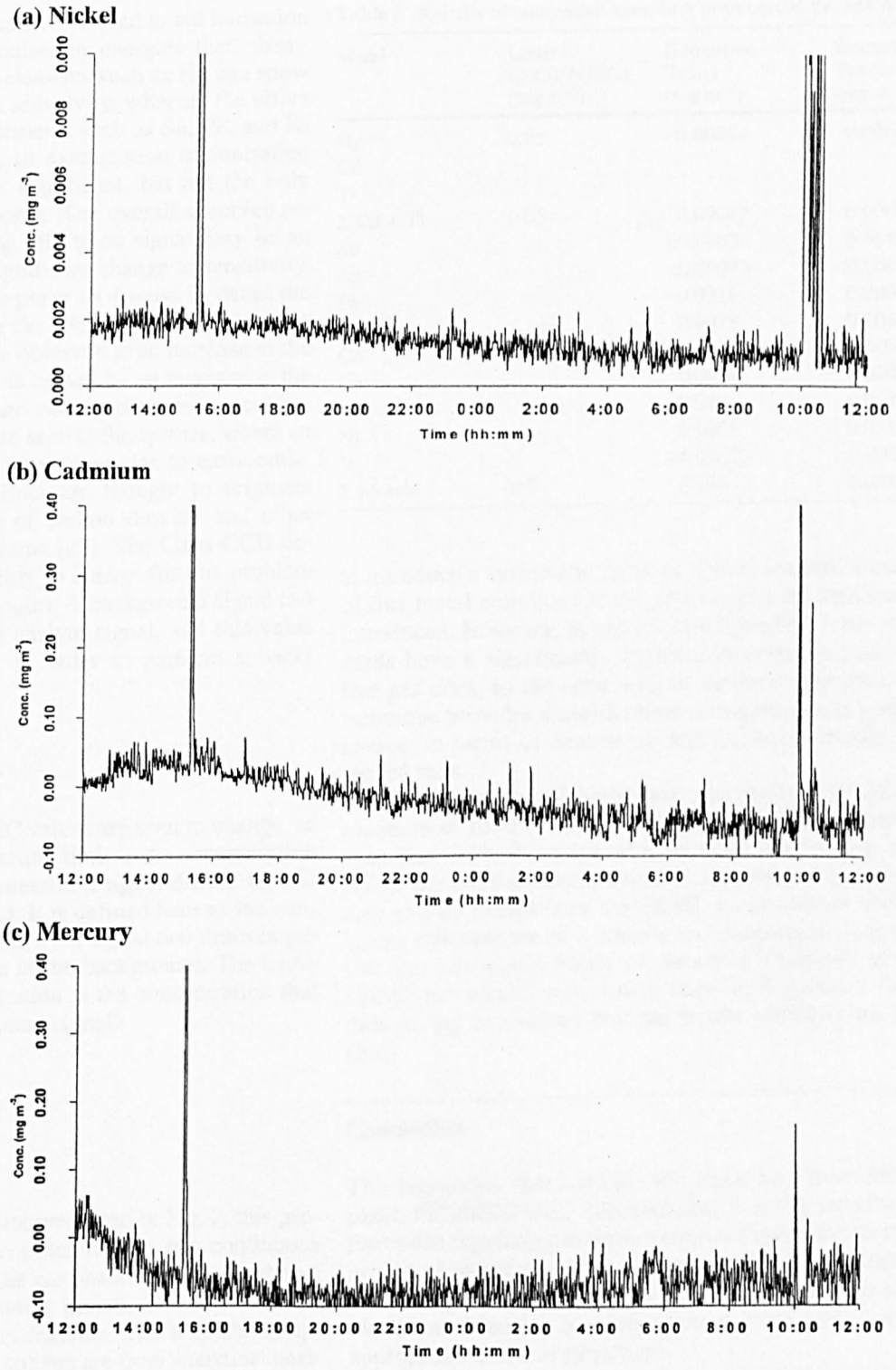


Fig. 7 Continuous measurement chart for nickel, cadmium and mercury

The calibration lines show two distinct features, which are both related to the effects on the plasma of carbon dioxide. The first phenomena is that for the calibration performed with elevated levels of carbon dioxide, the gradient of the calibration line differs compared with that of the atmospheric air calibration. Aluminium and nickel show signal enhancement whereas vanadium exhibits signal suppression. The effect on mercury is small, but shows a slight enhancement.

There are two main reasons for signal sensitivity change due to increased carbon dioxide in the plasma. The first is the quenching effect of the molecular gas, which will reduce the plasma temperature. As plasma temperature drops, the Boltzmann energy distribution of elements in the plasma will change. In particular, high upper-energy transitions will become less accessible, so signals corresponding to high-energy (ionic) transitions will tend to be suppressed [24]. The second effect is that of ionic species

generated, such as C^+. These are believed to aid ionisation of elements with lower ionisation energies than themselves. Thus hard to ionise elements such as Hg can show significant enhancement in sensitivity, whereas the effect on more easily ionisable elements such as Sn, Pb, and Ni is less [25, 26]. However, an examination of ionisation energies shows that this is significant, but not the only factor affecting signal response. The overall observed result of these two competing effects on signal may be an increase, decrease, or no significant change in sensitivity, but it is not the aim of this paper to discuss in detail the thermodynamic reasons for the effect on each element.

The second phenomenon observed is an increase in the value of the intercept. This is caused by an increase in the background noise at higher carbon dioxide concentrations. Evidence of this is also seen in the spectra, where an increasing carbon dioxide level gives rise to extra emission lines. The emission lines are thought to originate from molecular emissions of carbon dioxide and other species produced in the plasma [27]. The Ciros-CCD detector allows improved ability to correct for this problem over older detector technologies. A background signal can be taken to the side of the analyte signal, and this value subtracted from the peak, in order to perform a background correction.

Limits of detection

Limits of detection and BEC values are seen to change, as shown in Table 4. The detection limit is the concentration that is obtained when the measured signal differs significantly from the background. It is defined here as the concentration that corresponds to a net signal two times larger than the standard deviation of the background. The background equivalent concentration is the concentration that corresponds to the background signal.

Continuous measurements

Trace metals

As can be seen from the data presented in Fig. 7, this project has demonstrated the potential for the continuous measurement of metals in the gas phase. The results shown are taken from a 24-h sampling period. The charts shown in Fig. 7, show two distinct features. These spikes at approximately 15:30hrs and 10:00hrs are from analytical quality standards that were used to check the accuracy of the calibration. Differences in the sensitivity of the emission lines can be seen in the shapes of the peaks, with cadmium giving significantly narrower peaks than the more sensitive nickel.

It should be noted that the responses do not appear to be related to interferences from carbon dioxide emission, and that as such observed variations in signal response do correspond to changes in flue metal concentration. It is evident that the on-line calibration check has the potential to introduce a systematic error, as it does not take account of flue metal emissions at the point where the standard is introduced. However, as can be seen from Fig. 7, the standards have a significantly higher concentration than the flue gas does, so the error will be minimal, and thus this technique provides a useful check of measurement performance, in terms of sensitivity and accuracy, during extended runs.

Table 5 Results of alternative sampling protocols at the MSWI

Metal	Limit (2000/76/EC) ($mg\,m^{-3}$)	Extractive Test 1 ($mg\,m^{-3}$)	Extractive Test 2 ($mg\,m^{-3}$)
Hg	0.05	0.00014	0.00016
Cd			
Tl			
Σ Cd + Tl	0.05	*0.00047*	*0.00026*
Sb		<0.00073	*0.0041*
As		<0.00073	<0.00074
Pb		0.0015	0.00074
Cr		0.0018	0.0048
Co		<0.00022	<0.00022
Cu		0.0058	*0.00074*
Mn		0.080	0.0020
Ni		0.0061	0.021
V		<0.00022	<0.00022
Σ Metals	0.5	0.096	0.034

The data shown in Table 5, shows the results of the MSWI plants most recent legislative flue gas analysis. It can be seen that for both analytical tests plant is operating well below the required limit, which is also shown. Using this data and the results from the CEML it can be seen that the values obtained are of a comparable magnitude. And also that the calculated limits of detection (Table 4) of the CEML are significantly lower than the legislative limit, thus giving confidence that the results obtained are reliable.

Conclusion

The legislation that controls the emissions from MSWI plant, EC 2000/76/EC indicates that it is the intention of European regulatory bodies to introduce continuous monitoring of metal when the technology becomes available. The data presented here shows that the technique is capable of continuously measuring the desired metals at the appropriate limits of detection.

From the data presented in this work it has been shown that it is possible to quantitatively measure emission concentrations for elements in the gaseous emissions from an MSWI plant using ICP-OES. It has also been shown that is it possible to look at processes occurring in the gas and particulate phases. Furthermore, by adjusting the sampling time, it will be possible to adjust the resolution accordingly.

In continuing the development of the CEML system, and building on the work carried out to date, investigation

will continue by widening the range of elements under investigation and identifying the best emission lines for use with this instrument, for the unusual sample matrix of a gas which has significantly variable bulk composition. In doing this not only will the quality of the information obtained from the system improve but also knowledge will be gained that will be beneficial in developing the system further. This will lead to the validation of the method, and the demonstration of accuracy and reproducibility by comparison with approved analysis methods.

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Appendix 2: Analysis of MSW Incinerator Residues for Metals by ICP-OES

1.1 Introduction

This analytical method describes the preparation and analysis of solid residues remaining from municipal solid waste for heavy metals by ICP-OES.

1.2 Sample Preparation

Reagents, Materials and Equipment

The following materials were used in the preparation and analysis of samples:

- High purity distilled or deionised water
- Metal stock solution of 20 μg/ml (in 2 % HNO_3, prepared from the nitrate,). Used in the preparation of calibration standards
- Alternative stock 20 μg/ml metal calibration standard (Bernd Kraft GmbH Salze & Lösungen, Duisburg, Germany)
- High purity nitric acid (69% (m/v)) Aristar grade (Merck/BDH, Merck House, Poole, Dorset, UK).
- High purity hydrochloric acid (70% (m/v)) Aristar grade (Merck/BDH, Merck House, Poole, Dorset, UK).
- Graduated 15 or 50 ml test tubes (Sarstedt Ltd, 68 Boston Road, Beaumont Leys, Leicester, UK).
- Teflon beakers(SLS, Ruddington Lane Nottingham, UK).
- Cross-beater rotary mill (Model 16-150, Glen Creston Ltd, Middlesex, England)
- Thermal 6-Sample Digester (Fisher Scientific, Loughborough, UK).
- 4-figure digital electronic balance.
- ICP-OES (Spectro Ciros CCD)

Pre-Preparation of Laboratory Samples

The raw sample is thoroughly mixed, coned and quartered, and divided into two equal portions. Half of the sample is retained, with the other half being ground using a cross-beater rotary mill (Model 16-150, Glen Creston Ltd, Middlesex, England), until it is small enough to pass through a 0.5 mm mill mesh. For samples with a large initial particle size, multiple milling stages may be required. The ground material is mixed, and stored in sealed plastic containers. Laboratory sub-samples are taken in 50ml polypropylene sample tubes for analytical purposes.

Preparation of Samples

Two strong acid digestion methods may be used, both of which are digestions using a mixture of concentrated hydrochloric and nitric acids (aqua regia). The first is a conventional thermal digestion, where the samples are boiled in the acid mixture in an electrical heating unit. The second is a microwave-assisted sealed tube digestion, which had the advantage of offering more "harsh" digestion conditions but is only capable of using a smaller sample.

Thermal Digestion
2.0 g samples of solid are weighed accurately on a 4-figure balance, and placed in the acid-rinsed 350 ml pyrex tubes of a Büchi 6-Sample Digester (Fisher Scientific, Loughborough, UK). 15ml of hydrochloric acid is added, followed by 7.5ml of nitric acid, and the samples were boiled for 2 hours. The temperature is maintained such that a reflux is maintained on the tube sides, which are air cooled, to conserve the sample volume. The samples are periodically agitated, to ensure that the whole of the solid sample is exposed to the acid mixture. If loss of acid volume is noted, further acid may be added as required, after allowing the tubes to cool

Microwave Assisted Digestion
Samples are digested using an Anton Paar Multiwave 3000 microwave digester (Anton Paar, Hertfordshire, UK). 8 samples were digested simultaneously. 0.5g of solid is weighed accurately on a 4-figure balance, and placed in the acid-rinsed digestion vessel. 6 ml of nitric acid is added, followed by 1ml of hydrochloric acid. The samples are placed in the microwave, and were microwaved at 1400w, ramped linearly from zero over 5 minutes, and held at full power for 20 minutes.

Sample Preparation for Analysis
Digested samples (from either digestion method) are allowed to cool, filtered or centrifuged to remove or compact any insoluble material, and diluted to 50 ml with de-ionised water. These samples are collected in 50ml polypropylene tubes, and stored at room temperature prior to analysis by ICP-OES. For major constituents (e.g. aluminium, calcium, sodium), 10-fold, 100-fold or even 1000-fold dilution of the initial sample may be required, to obtain concentrations in the range measurable by the instrument.

1.3 Sample Analysis

Instrumentation - ICP-OES
Metals are determined at the optimum emission lines for the elements under investigation using a Spectro Ciros^{TM} CCD ICP Atomic Emission Spectrometer with radial viewing configuration. The sample introduction system consists of a Modified Lichte nebuliser and a glass spray chamber. Main operating parameters are (nominally): forward power, 1400 W; plasma gas flow, 12 l/min; auxiliary gas flow, 1.0 l/min; nebuliser gas flow, 0.9 l/min. Samples, which are manually introduced, are initially aspirated for 20 seconds at a relatively high pump speed (pump speed 4), and then the system is stabilised for 20 seconds (pump speed 2, equating to ~ 2 ml/min) prior to measurement. Data acquisition is based on measurement in the "quantification mode" with simultaneous on and off peak measurement (for background correction). The instrument determines signal integration times automatically and three replicate measurements along with their mean are acquired for each sample solution.

1.4 Calibration

Standard Solutions
The following calibration standard solutions, outlined in the table below, are prepared by serial dilutions of the stock solutions with appropriate additions of 10%HNO_3.

Table 1: Calibration standard solutions

calibration standard	element concentration (ng/ml)
1	0
2	10
3	100
4	500
5	1000
6	5000
7	10000

These standards are introduced into the ICP instrument to establish calibration curves.

ICP-AES Calibration

The calibration curves are constructed as the Element signal versus concentration and expressed as $y = mx + c$, where y = Element emission in cps, x = Element concentration and m is the calculated slope. A calibration curve is prepared before analysis commences, and checked at the end of the analysis run.

Raw Data

Once prepared all samples are analysed by ICP-AES. Results are stored electronically and in paper form.

Appendix 3: Quantification of USN Transport Properties

Introduction

In normal analysis of liquids by ICP-OES, the exact efficiency and aerosol formation parameters of the nebuliser do not need to be known, as it may reasonably be assumed that the calibration standards and samples, all of which are liquids, are nebulised with similar efficiency. However, in order to quantify gas-phase metal concentrations, the gas-phase standard concentration arising from the introduction of liquid standards to the nebuliser must be accurately known. This is achieved through a simple mass-balance calculation on the device.

Calculation Procedure

There are three inputs to the nebuliser, and 3 outputs.

The inputs are of liquid calibration standard, flue gas, and nebuliser argon. The outputs are an aerosol to the ICP, and spray chamber and condenser liquid waste.

The gross efficiency of aerosol production is simply calculated by determining the mass of calibration standard consumed per unit time (which does not end up in either waste stream), and dividing by the known gas flows through the ICP:

$$C_{aer} = \frac{(Mass_{CS} - Mass_{SW} - Mass_{CW})}{(Volume_{SG} + Volume_{Ar})}$$

Where

	C_{aer}	is the aerosol concentration (mgm^{-3})
	$Mass_{cs}$	is the mass of calibration standard used (mg)
	$Mass_{sw}$	is the mass of spray chamber waste produced (mg)
	$Mass_{cw}$	is the mass of condenser waste produced (mg)
	$Volume_{sg}$	is the volume of sample gas flowing through the nebuliser (m^3)
and	$Volume_{Ar}$	is the volume of nebuliser argon flowing through the nebuliser (m^3)

Thus a gas-phase concentration of calibration standard solution is obtained, from which the concentration of an individual metal is easily calculated from the proportion of that metal in the standard (i.e. a 20 ppm standard has 20mg of metal in 10 000 000 mg of liquid and thus the aerosol concentration of metal is $2x10^{-6}$ lower than that of the aerosol as a whole). Typically, when determining aerosol density experimentally, 3 repeat measurements are made, each lasting 5-10 minutes, to improve the calculation accuracy, as the nebuliser efficiency can vary somewhat over time, and varying transport of liquid wastes out of the nebuliser can affect the mass-balance values obtained.

Although this calculation can be perfectly acceptable ordinarily, it does not account for the fact that the nebulisation efficiencies of the metals in a standard solution can be markedly different from that of the carrier solution itself. Thus improved accuracy may be obtained if the wastes obtained are analysed by ICP-OES, and the mass balance for metals, rather than total solution mass, is obtained. Although a more

involved and lengthy process, this has been found to be worthwhile, with the basic calculation remaining the same, only with the concentration of metals in the wastes being quantified. This is the method used in the results reported in the thesis. Efficiencies actually vary a little from metal to metal, but an average for all analytes is usually used.

Appendix 4: Quantification of Sampling System Transport Properties

Background

In all analytical systems the collection and preparation of the sample is the key to the delivering accurate and reproducible results. The taking of gas samples is difficult for several reasons, not least of which are the effects of temperature and pressure on the sample volume. There was therefore a need to characterise the sample line and understand the sampling process used in the CEML.

In the original instrumental configuration for the CEML, a needle-valved, flow meter was located between the primary pump and the secondary sampling head. Initial investigations showed that if the flow meter was set to 100L min^{-1}, the flow at the sample point would read 20-30L min^{-1}. This apparent anomaly has led to a study of the heated sample line, in an attempt to understand the mechanisms that are involved in the sampling process. The following section will show, however, that this is not an anomalous measurement, but is a function of the physical properties of the gases.

Theory

The sample collection system for the CEML is shown in Figure 1. The values shown are typical for the system in whilst connected to the test rig at the Harpur Hill Research Station in Buxton. At the test site the typical temperature of the flue gas at the sampling point is 300-500°C, whereas at a MSW incinerator, the temperature would typically be 130°C.

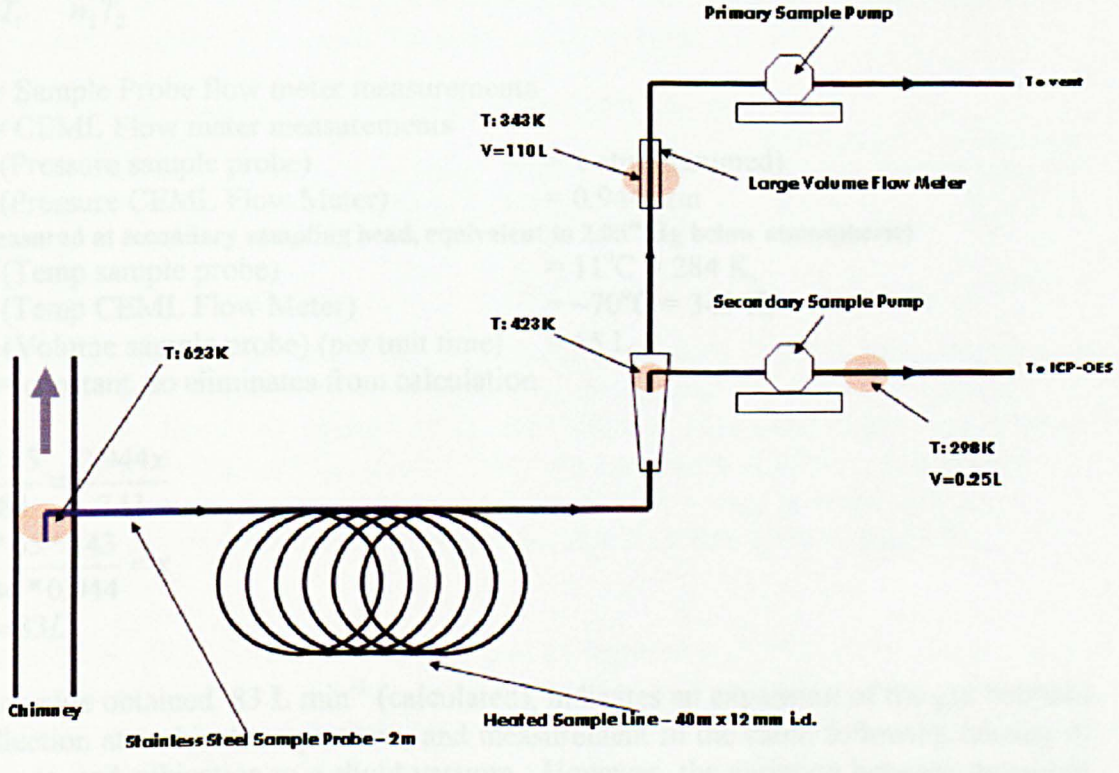

Figure 1: Schematic diagram showing the sample collection system with flow and temperature measurement points

Conservation of Matter
In a closed system, matter cannot be created or destroyed. In this system, a constant mass of matter enters and leaves the system per unit time. However, as we shall see, the volume of the matter need not remain constant, as temperature and pressure change, and this has an effect on the amount of matter taken at the point of secondary sampling.

Charles's law: V α T (at constant pressure)
When a gas is heated, it increases in volume in proportion to its temperature. When the flow was measured at the sampling end of the sample line, the furnace was off, and ambient air was used as the sample gas. Thus when the gas was heated within the sampling line, expansion occurs. Therefore, when the flow rate (i.e. volume of flow per unit time) was measured inside the CEML, at 70°C, the value had increased from that measured at the start of the sample line.

Boyle's Law: p α 1/V
Although both the sample inlet and exhausts are subject to the same atmospheric pressure, a reduced pressure is experienced in the pipe at the CEML end, due to the effect of the primary pump, and the resistance to flow caused by the length of the sampling pipe.

The Combined Gas Law:
Illustrative Calculation
The theory was tested by measuring temperature and volume at both the sample probe tip and at the CEML flow meter, when the probe was sampling ambient air.

$$\frac{p_1V_1}{n_1T_1} = \frac{p_2V_2}{n_2T_2}$$

1 = Sample Probe flow meter measurements
2 = CEML Flow meter measurements
p_1 (Pressure sample probe) = 1 atm (assumed)
p_2 (Pressure CEML Flow Meter) = 0.944 atm
(measured at secondary sampling head, equivalent to 2.05" Hg below atmospheric)
T_1 (Temp sample probe) = 11°C = 284 K,
T_2 (Temp CEML Flow Meter) = ~70°C = 343 K,
V_1 (Volume sample probe) (per unit time) = 65 L
n = constant, so eliminates from calculation

$$\frac{1*65}{284} = \frac{0.944x}{343}$$
$$\frac{1*65*343}{284*0.944} = x$$
$$x = 83L$$

The value obtained, 83 L min^{-1} (calculated), indicates an expansion of the gas between collection at ambient temperature, and measurement in the cabin following heating of the gas, and subjection to a slight vacuum. However, the variation between measured (110 L min^{-1}) and calculated (83 L min^{-1}) flow rates, indicates that the measurements and theory presented so far do not fully explain the observed phenomenon of apparent gas expansion.

Rotameter Measurement Density, Temperature and Pressure Correction

The flow meters used were designed to work for specific gases under specified temperatures and pressures, which were not always the same as measurement conditions. If measurements are made other that at Atmospheric Temperature and Pressure (ATP), the standard conditions specified, then mathematical corrections must be made for the measurement of a different gas from the one specified for the device, and for measurements at different temperatures and pressures.

$$F_{true} = \frac{F_{Meas,G}}{K}$$

Where F_{true} is the true flow rate (L min^{-1}) at the temperature and pressure measured, $F_{meas,\,G}$ is the measured flow rate (L min^{-1}) for a specific gas rotameter under those conditions, and K is a "sizing factor" evaluated as follows:

$$K = \sqrt{R \frac{T_2}{P_2} \frac{P_{std}}{T_{std}}}$$

Where R is the relative density of the measured gas (relative to air), T_2 and P_2 are the Temperature and Pressure of the gas as measured respectively, and P_{std} and T_{std} are the standard specified measurement conditions for the rotameter in question, usually 1.013 Bar and 293 K.

It will be noted that the expression includes the temperature and pressure corrections as in our previous calculations, and also a density correction not yet considered. These equations were used to calculate the actual flow rate encountered at the measurement points, which gave rise to the observed measurements. The results were also standardised to ATP, to see what the standardised "true" flow at the two measurement locations would be. The results are summarised in Table 1.

Table 1: Flow parameters at different points in the CEML sampling system

location	measured flow rate (L min^{-1})	pressure P_{meas} (atm)	sizing factor correction, K	relative density, R	temp T_{meas} (K)	sizing factor corrected flow of gas (L min^{-1})s	Actual flow of gas at ATP (L min^{-1})
pump end	110	0.944	1.121	1	343	98.14	78.13
probe end	65	1.013	0.838	0.725	284	77.54	80.00

Thus it can be seen that observed measurements of flow of 65 L min^{-1} atmospheric temperature air (measured with an argon flow meter), and 110 L min^{-1} (measured with an air flow meter at about 70°C) are entirely consistent with one another, corresponding to the same "absolute" flow. An agreement of 97% is obtained between the two measurements for the absolute flow at ATP, which is reasonable, given the error associated with the measurements (typically 2%), due to fluctuations in both flow and temperature.

Nevertheless, in this example it is seen that an expansion of 27% of the actual volume of sample gas does indeed occur between the start and end of the sample line when measuring ambient air. This would account for a drop in measured concentration of an analyte of about 30%, if the flue gases were at ambient temperature when sampled, and the conditions in the secondary sampling head were the same as those measured at the rotameter.

Gas Volume Correction under Measurement Conditions

Thus the question arises as to what changes in sample volume are occurring between flue sampling point, secondary sampling, and ICP measurement, when measurements are being made. An extensive study of the temperature, pressure and volume profile of the sampling system was undertaken, the results of which are shown in Figure 1. In this situation, where the sample removed from the flue is at higher temperature and pressure than at the point of removal of the secondary sample, there is a fall in sample volume between collection and secondary sampling, and so an effective pre-concentration of analyte concentration per unit volume. Again, the sample removed from the secondary sampling device is at a higher temperature than that reaching the ICP, so there is further effective pre-concentration in the secondary sampling line. The effects on sample volume are summarised in Table 2.

Table 2: Sample line volume corrections for Buxton furnace measurements

location	measured flow rate ($L\ min^{-1}$)	pressure P_{meas} (atm)	sizing factor, K	R, relative density	temp. T_{Meas} (K)	corrected flow ($L\ min^{-1}$)	actual flow at ATP ($L\ min^{-1}$)	enrichment factor
flue	208 L	1.013	1.24	0.73	623	168 L	79 L	
secondary sampling	130 L	0.944	1.06	0.73	423	123 L	79 L	1.37
secondary sampling	240 mL	0.944	1.06	0.73	423	226 mL	146 mL	
secondary pump	150 mL	1.013	1.01	1.00	298	149 mL	146 mL	1.52

Conclusion

Using the combined gas law, with measurement correction factors for gas temperature and density, it is possible to determine accurately the volume of gas being sampled and thus provide essential information for the calculation of the metal concentration of the sample. Apparent anomalies can be explained using physical laws.

Previously, under our standard measurement conditions at the Buxton research site, a sample line volume correction factor (enrichment) of 0.355 was calculated, using the combined gas law alone, without measurement correction factors. Along with the known dilution of the gas sample with argon in the nebuliser, a factor of 5.83, a total sample volume correction factor (dilution) for gas analysis was obtained, of 2.07, indicating an expected two-fold drop in sensitivity between calibration and measurements, due to the different sample parameters experienced. This figure is dependent on sampling temperature, the speed setting of the secondary pump, and the argon settings for nebuliser and additional flow on the ICP. Accordingly, if any of these are modified, the sample correction factor must be re-evaluated.